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**MEMOIRS** OF THE

**I**nstitute of  
**S**cientific and  
**I**ndustrial  
**R**esearch



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## **Foreword**

### **For the development of “Honorable Science” and “Advantageous Technology”**

**Akihito Yamaguchi**

**Director, The Institute of Scientific and Industrial Research**

The Institute of Scientific and Industrial Research (ISIR), Osaka University was founded in 1939, 68 years ago, with only 3 departments by the financial support from Industries of Kansai area to promote basic science for the development of industry. From then, ISIR has emphasized basic and applied researches to promote the multidisciplinary science for ultimate contribution to the industries in 3 main research areas, i.e., material science, information science, and bio-sciences. At present, we have 7 divisions including 28 departments and 3 research Centers, "Nanoscience and Nanotechnology Center", "Materials Analysis Center" and "Materials Science & Technology Research Center for Industrial Creation". "Nanoscience and Nanotechnology Center" is focusing the researches on advanced materials and devices, beam-science for nanotechnology which is key technology now and future and then it's one of the leading research organizations in Japan.

ISIR has also close contact with several faculties of Osaka University such as Faculties of Science, Engineering, Engineering Science, Pharmaceutical Science, Information Science and Technology, Frontier Biosciences, and supervises their graduate students. From 2002 through 2006, the Institute was selected as the 21st Century COE in the fields of new and interdisciplinary area.

This publication "Memoirs of the Institute of Scientific and Industrial Research (ISIR)" is our annual publication summarizing the scientific activities of ISIR. We have particulate plan for the future, and our challenges are never ending. We hope this annual publication will be useful and stimulating for all researchers and young scientists outside as well as inside our Institute.

ISIR will continue to make contributions to the development of industry through basic science and technology and inspire the future.

## **Outline of ISIR**

### **1. Research Activities**

#### **1) History and Organization**

The Institute of Scientific and Industrial Research (ISIR) was founded in 1939 as a part of Osaka University, based on the strong desire of the business leaders of private enterprises in Osaka area. The purpose of the Institute is to study science necessary for industry and their applications. Since then, the institute had developed into one of the leading research organizations for science and engineering in Japan.

In 1939 ISIR had only 3 departments, however it had increased research areas and laboratories in the fields of electronic engineering, computer science, metallurgy and inorganic chemistry, organic chemistry, biochemistry, and beam science.

Modern industry in this country is, however, coming to a major turning point. There is a strong requirement to develop interdisciplinary sciences, or new fields which are away from conventional area in order to advance basic and applied sciences coping with social changes.

Since this Institute has researchers in a wide variety of fields and is suitable for making a new organization for interdisciplinary areas, it was restructured in 1995 to an Institute with 6 divisions with 24 departments for the purpose of promoting sciences on materials, information and biology. For solving problems related to energy, earth ecology, aging and advanced information technology, interdisciplinary and comprehensive studies have been conducted in the Institute. From 2002 through 2006, we have awarded as the best group in 21st Century COE program that is originally the top 20 group plan in Japan. This involves the positive exchange between different laboratories which yield results of the global level with respect to material, information and biotechnology.

In 2002, Nanoscience and Nanotechnology Center has started with restructuring Research Center for Intermaterials and Radiation Laboratory. The new Center focuses its researches on nanomaterials and devices, beam science for nanotechnology and industrial nanotechnology. In 2006, Materials Science & Technology Research Center for Industrial Creation has started and at present, ISIR has 7 divisions including 28 departments and 3 research Centers, "Nanoscience and Nanotechnology Center", "Materials Analysis Center" and "Materials Science & Technology Research Center for Industrial Creation". In April 2006, Academia Industry Relation Office (AIR-Office) has been settled in order to strengthen cooperation between the Institute and Industries.

|           |
|-----------|
| Divisions |
|-----------|

|             |
|-------------|
| Departments |
|-------------|

**Quantum Engineering**

Quantum Molecular Devices  
Photonic and Electronic Materials  
Semiconductor Electronics  
Condensed Matter Physics

**Advanced Materials  
Science & Technology**

Structural Characterization and Design  
Metallic Materials Process  
Atomic Scale Science  
Functional Ceramic Materials  
Structure Ceramic Materials  
Advanced-Energy Materials

**Organic Molecular Science**

Regulatory Bioorganic Chemistry  
Organic Fine Chemicals  
Organic Molecular Materials  
Molecular Excitation Chemistry  
Synthetic Organic Chemistry  
Analytical Molecular Chemistry

**Intelligent Systems Science**

Knowledge Systems  
Intelligent Media  
Architecture for Intelligence  
Advanced Reasoning

**Biological Science**

Structural Molecular Biology  
Single Molecule Biophysics  
Cell Membrane Biology

**Quantum Beam  
Science & Technology**

Accelerator Science  
Beam Materials Science

**Next Industry Generation**

New Industrial Projection  
New Industry Generation Systems  
Intellectual Property Research

---

**Research Centers****Nanoscience and  
Nanotechnology Center**

**Nanomaterials and Nanodevices**  
Artificial Nanomaterials for Bio-Information  
Systems  
Single-Molecular Integrated Devices  
Supramolecular Chemistry  
Nanobiology  
Nanosystem Design

**Beam Science for Nanotechnology**

Beam Science and Nanofabrication  
Quantum Beams for Nanotechnology  
Beam Processing for Nanotechnology  
Ultrafast Spectroscopy of Nanostructures

**Nanoscience and Nanotechnology for Industrial Applications**

Nanomaterials and Environmentally Conscious Technology  
Computational Nanomaterials Design  
Nano-Bio-Intelligent Systems Science  
Nanotechnology Transfer

**Nanocharacterization**

Advanced Nanostructural Characterization  
Advanced Characterization for Nano-Processing  
Quantum Materials and Devices Characterization

**Open Laboratory**

**Radiation Laboratory**

**Electron Microscope Laboratory**

**Electronic Processing Laboratory**

**Nanofabrication Shop**

**The Handai Multi-Functional Nanofoundry**

**Materials Analysis Center**

**Materials Science & Technology  
Research Center for Industrial  
Creation**

**Materials Research Project**

Hard Materials Research Group  
Soft Materials Research Group

**Human Interface Research for Safety and  
Security Project**

Medical Sciences Research Group  
Human Interface Research Group

**Post-Silicon Materials and Devices Research Alliance**

**Service Facilities**

**Workshop**

**Office of Information Network**

**Laboratory for Radio-Isotope Experiments**

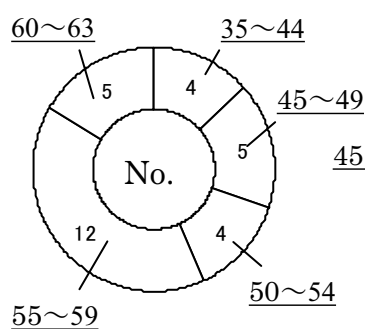
**Library**

**Academia Industry Relations Office**

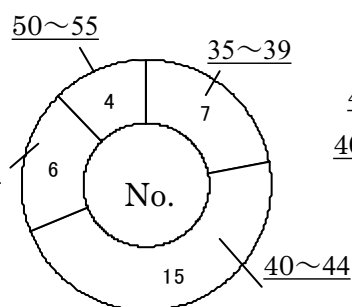
**Public Relations Office**

### Staffs' Age (years old) –As of 3.31.2008

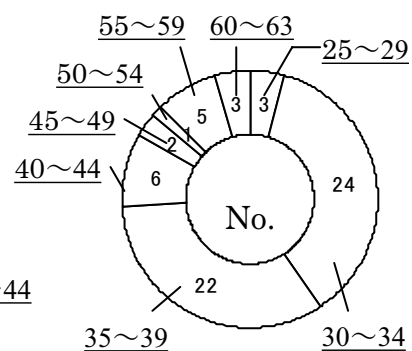
#### Professors



#### Associate Professors

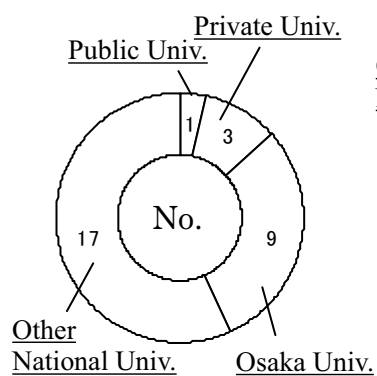


#### Assistant Professors

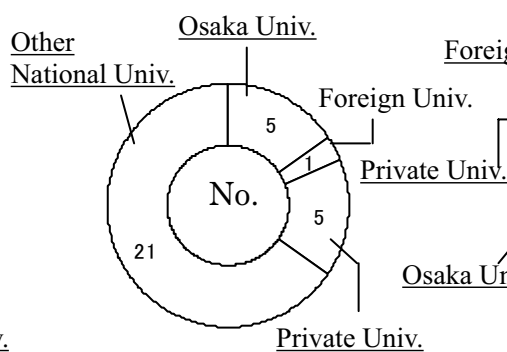


### Staffs' Alma Mater –As of 3.30.2008

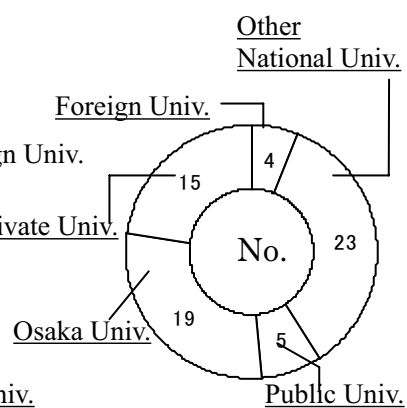
#### Professors



#### Associate Professors



#### Assistant Professors





## 2) Administration

Administration and management of ISIR are conducted by the Director elected from the full professors of ISIR. The term of the Director is two years. Reappointment is possible, but the Director cannot be in the position for more than four years. Professor Tomoji Kawai had been a Director till March 31, 2008 and Professor Akihito Yamaguchi has been a Director since April 1, 2008.

Important matters of ISIR are discussed and determined by the Faculty Council, which consists of the Director and all professors of ISIR. Various committees such as International Exchange, Self-Review, Circumstances and so on are working for each purpose.

Administration of the Institute-associated Centers is conducted by Director of each Center and its Executive Committee.

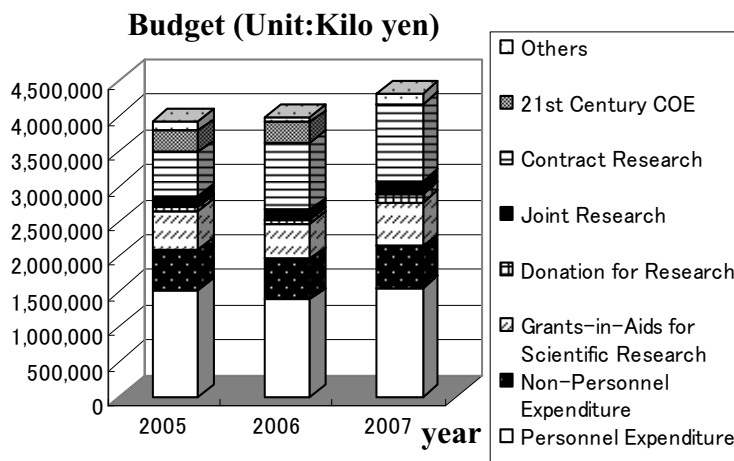
Evaluation Committee composed of outside experts in academic societies was established and the committee evaluated several items such as management, budget, facilities and research activities.

The new organization was highly evaluated, but with change of their structure to National University Agencies in April 2004, our management system needs reshaping. A Board of Directors under the Director has been formed, and Advisory Board has been set up to introduce opinions from outside into the Institute.

## 3) Research Budget

The budget of ISIR is mainly composed of Subsidy for operating expenses, Grants-in-Aid for Scientific Research of Ministry of Education, Sports, Culture, Science and Technology, Donations for Research, and Budget of Joint Research. The recent trend in the expenditure of ISIR is as follows.

Grants-in Aid for Scientific Research of Ministry of Education, Culture, Sports, Science and Technology are delivered to researchers and the total budget in 2007 is 634,747yen.



## Donation for Research

Donation for Research is accepted after the Judgement of Committee and the amount in these three years are as follows.

(Unit : kilo yen , (    ) Number)

| Division<br>Year | Quantum<br>Engineering | Advanced<br>Materials Science<br>and Technology | Organic Molecular<br>Science | Intelligent<br>Systems Science |
|------------------|------------------------|-------------------------------------------------|------------------------------|--------------------------------|
| 2005             | 2,200<br>( 3)          | 12,440<br>(16)                                  | 10,830<br>(14)               | 13,930<br>(10)                 |
| 2006             | 4,500<br>( 3)          | 13,141<br>(17)                                  | 16,400<br>(13)               | 10,100<br>(8)                  |
| 2007             | 500<br>(1)             | 22,600<br>(18)                                  | 34,999<br>(20)               | 19,614<br>(0)                  |

| Division<br>Year | Biological<br>Science | Quantum<br>Beam<br>Science and<br>Technology | Nanoscience and<br>Nanotechnology<br>center | Others         | Total           |
|------------------|-----------------------|----------------------------------------------|---------------------------------------------|----------------|-----------------|
| 2005             | 1,833<br>( 3)         | 0<br>(0)                                     | 25,690<br>(18)                              | 1,950<br>( 6)  | 68,873<br>(70)  |
| 2006             | 9,250<br>( 7)         | 0<br>(0)                                     | 10,700<br>( 9)                              | 13,300<br>( 5) | 77,391<br>(62)  |
| 2007             | 11,350<br>(10)        | 1,600<br>(2)                                 | 17,570<br>(16)                              | 300<br>(1)     | 108,533<br>(78) |

## 4) Cooperative Research

Cooperative Researches and Contract Researches in the fiscal year 2007-2008 are as follows: Cooperative Researches are carried out with 72 organizations. The budget for the fiscal year 2007-2008 is 192,883,000 yen. Contract Researches are 63. The budget for the fiscal year 2007-2008 is 1,082,598,000 yen.

## 5) International Research Projects

Tomoji Kawai                      Core University Program (CUP) between Japan and Korea  
(Director of the                      (Joint Research Projects under the Bilateral Programs between  
operating organization) JSPS and KOSEF).

Tohru Sekino/Tetsuro              "New Processing and Nanostructure/Property Relationship for  
Majima (Coordinator)              Multi-functional Ceramic Materials" (in the field of Ceramic  
Materials Technology)  
Hanyang University (Counter Core University in Korean Side)

|                    |                                                                                                                                                                                                                                                      |
|--------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Riichiro Mizoguchi | Japan Partnering Award (The Biotechnology and Biological Sciences Research Council in Britain)<br>"Advanced Scientific Discovery Tools for Bioinformatics"                                                                                           |
| Satoshi Murakami   | Strategic International Cooperative Program/United Kingdom<br>"Functional Analysis of Multi-Drug Efflux Transporter Based on the Crystal Structure"<br>Hendrik Willem van Veen, Senior Lecturer, Department of Pharmacology, University of Cambridge |

## 6) Symposia, Seminars, Workshops and Lectures

|           |                                                                                                                                                                                                                                                                                    |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 3-Jul     | The workshop on new photocatalysts (No.1/'07-'08)                                                                                                                                                                                                                                  |
| 27-Jul    | The first regular meeting of the workshop on new semiconductor chemical processes                                                                                                                                                                                                  |
| 18,19-Aug | Seminar on Molecular Nano-Mechanics & Bio-Mechanics Research Group (G3) of Post-Silicon Materials and Devices Research Alliance                                                                                                                                                    |
| 27-Sep    | Seminar on New Functional Nano-Electronics Research Group (G2) of Post-Silicon Materials and Devices Research Alliance                                                                                                                                                             |
| 2-Oct     | Seminar on Molecular Nano-Electronics Research Group (G1) of Post-Silicon Materials and Devices Research Alliance                                                                                                                                                                  |
| 30-Oct    | The Workshop on porous materials(No.1/'07-'08)                                                                                                                                                                                                                                     |
| 2-Nov     | Joint Symposium between ISIR, Osaka University and Institute of Industrial Science, the University of Tokyo                                                                                                                                                                        |
| 16-Nov    | A symposium on a special topic and a subsequent conference for presenting results of research activities made by the members of the Institute are held annually in November. They are open to the public. The topics in 2007:"Knowledge of Frontier Cultivation and Globalization" |
| 22-Nov    | The second regular meeting of the workshop on new semiconductor chemical processes                                                                                                                                                                                                 |
| 7-Dec     | The workshop on new photocatalysts (No2/'07-'08)                                                                                                                                                                                                                                   |
| 9-Dec     | Hard Materials Research Symposium, Materials Science & Technology Research Center for Industrial Creation                                                                                                                                                                          |
| 14-Dec    | The 7th workshop on Radiation Laboratory -New Development of the Radiation Laboratory and Beam Science-                                                                                                                                                                            |
| 20,21-Dec | The 12th Symposium on the Physics and Application of Spin-Related Phenomena in Semiconductors (PASPS-12)                                                                                                                                                                           |
| 25,26-Dec | Symposium on 2007 Research Progress of Post-Silicon Materials and Devices Research Alliance                                                                                                                                                                                        |
| 6-Jun     | Commemoration Symposium on Post-Silicon Materials and Devices Research Alliance                                                                                                                                                                                                    |

|           |                                                                                                                                                                                                     |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 7~10-Jan  | The 17th JSPS-KOSEF Core University Program(CUP) Seminar in conjunction with The 9th International Symposium on Eco-Materials Processing and Design(ISEPD2008)                                      |
| 17-Jan    | 2007 Sanken Symposium, Materials Science & Technology Research Center for Industrial Creation                                                                                                       |
| 23-Jan    | The 8 <sup>th</sup> workshop on Radiation Laboratory –New Development of Chemistry by means of Beams-                                                                                               |
| 4,5- Feb  | 11 <sup>th</sup> SANKEN,6 <sup>th</sup> Nanotechnology Center and 1 <sup>st</sup> MSTEC International Symposium "New Advances in Nanoscience & Nanotechnology"                                      |
| 15-Feb    | The workshop on porous materials (No.2/'07-'08)                                                                                                                                                     |
| 22-Feb    | The workshop on new photocatalysts (No.3/'07-'08)                                                                                                                                                   |
| 27,28-Feb | Third SANKEN-Chungnam National University, Korea(CNU) Joint Symposium on Nanoscience and Nanotechnology                                                                                             |
| 5-Mar     | The workshop on porous materials (No.3/'07-'08)                                                                                                                                                     |
| 11-Mar    | 2007 Symposium, Materials Science & Technology Research Center for Industrial Creation                                                                                                              |
| 19-Mar    | The third regular meeting of the workshop on new semiconductor chemical processes                                                                                                                   |
| 13-Mar    | Symposium on Radiation Laboratory                                                                                                                                                                   |
| 27-Mar    | Joint Symposium between ISIR, Osaka University and the Faculty of Science, Chiang Mai University                                                                                                    |
| 31-Mar    | The workshop between ISIR, Osaka University and ISSP, the University of Tokyo -Present Status and Future Prospects of Advanced Beam Sciences- (ISSP in the Kashiwa Campus, the University of Tokyo) |

### Other Lectures and Seminars

|        |                                                                                                                                       |                                                                               |
|--------|---------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| 4-Apr  | Baldacchino Gerard<br>(Saclay Atomic Energy Research Center,Researcher)                                                               | "Primary Events in Radiation Chemistry under Extreme Condition of LET,T,P..." |
| 5-Apr  | Toru Okabe<br>(Baylor College of Dentistry,USA ,Professor)                                                                            | Application of easily-casted titanium alloys to dental materials              |
| 18-Apr | Felix Studt<br>(Center for Atomic-scale Materials Design (CAMD),<br>Department of Physics,Technical University of Denmark,Researcher) | Predicting Hydrogenation/Dehydrogenation Reactions from Scaling Relation      |
| 13-Jun | Vadim N. Gladyshev(Department of Biochemistry, Nebraska Redox Biology Center, University of Nebraska,Professor)                       | Selenoproteins:Roles in Redox Biology and Human Health                        |
| 15-Jun | Katsuyuki Shiroguchi<br>(Department of Physics, Waseda Univeristy,Assistant Professor)                                                | Single molecule study on power-stroke mechanism of myosin motor protein       |

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|--------|------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|
| 15-Jun | Masami Horikoshi<br>(Institute of Molecular and Cellular Biosciences<br>The University of Tokyo, Associate Professor)              | Toward the theory of gene regulation by chromosome                                                                                                 |
| 29-Jun | Hirotsune Watanabe<br>(Semiconductor Leading Edge Technologies, Inc. Representative executive)                                     | Discovery Science Expected in Semiconductor Industry                                                                                               |
| 29-Jun | Mitsuhide Matsushita<br>(JEOL Ltd. Junior Manager)                                                                                 | Advanced Transmission Electron Microscopy Techniques (1)                                                                                           |
| 29-Jun | Yoshihiro Arai<br>(Terabase Ltd. Executive)                                                                                        | Advanced Transmission Electron Microscopy Techniques (2)                                                                                           |
| 29-Jun | Kiyoshi Yase<br>(National Institute of Advanced Industrial Science and Technology (AIST), Deputy Director)                         | Organic Electronics and Photonics                                                                                                                  |
| 4-Jul  | Ayyappanpillai Ajayaghosh<br>(Photosciences and Photonics Group, Regional Research Laboratory (CSIR) Trivandrum, India, Professor) | Molecular Self-assemblies as Scaffolds for Excitation Energy Transfer                                                                              |
| 9-Jul  | Tetsuro Ogushi<br>(Hiroshima International university, Professor)                                                                  | Current status and perspective for application and development of Lotus-type porous metals<br>-application to heat sink of electronic instruments- |
| 9-Jul  | Seiichi Nagatome<br>(Kawasaki Heavy Industries, Ltd., Senior Counselor)                                                            | Current status and perspective for application and development of Lotus-type porous metals<br>-application to engine parts of aircrafts-           |
| 9-Jul  | Yuichi Higuchi<br>(Osaka Dental University, Lecturer)                                                                              | Current status and perspective for application and development of Lotus-type porous metals<br>-application to dental implants-                     |
| 10-Jul | Ayyappanpillai Ajayaghosh<br>(Photosciences and Photonics Group, Regional Research Laboratory (CSIR) Trivandrum, India, Professor) | Squaraine Dyes: Versatile Chromophores for the Design of Cation Probes and Nanoarchitectures                                                       |
| 24-Jul | Pavel Kocovsky<br>(University of Glasgow, Professor)                                                                               | Asymmetric Synthesis: From Transition Metals to Organocatalysis                                                                                    |
| 30-Jul | Hideo Horibe<br>(Kanazawa Institute of Technology, Professor)                                                                      | Research for EUV                                                                                                                                   |

|        |                                                                                                                                 |                                                                                                                                        |
|--------|---------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| 16-Aug | Dr. Jakob Mauss<br>(QTronic GmbH, Berlin,<br>Germany, Lecturer )                                                                | Modeling of complex physical<br>systems by Modelica language<br>based on differential equations and<br>finite state machines           |
| 17-Aug | Sergey V. Anishchik<br>(Institute of Chemical Kinetics &<br>Combustion, Russia , Professor)                                     | Time-resolved microwave field<br>effects in recombination<br>fluorescence from non-polar<br>solutions                                  |
| 20-Aug | Jiang-Yu Zheng (Indiana University<br>Purdue University<br>Indianapolis, Associate professor)                                   | Route Panorama for Cityscape<br>Visualization                                                                                          |
| 23-Aug | Marc Koper<br>(Universiteit Leiden, Professor)                                                                                  | Molecular Simulations of electric<br>Field and solvent effects at<br>electrochemical interfaces                                        |
| 14-Sep | Gensyu Fuse<br>(SEN Corporation, an SHI and Axcelis<br>Company, Chief Engineer)                                                 | Hot topics on LSI technology<br>-from VLSI Symposium-                                                                                  |
| 19-Sep | Takeaki Uno<br>(National Institute of Informatics,<br>Associate Professor)                                                      | Pattern Retrieval Under Ambiguous<br>Condition                                                                                         |
| 26-Sep | Jioon Ihm<br>(Seoul National University, Professor)                                                                             | Combinatorial search and<br>computational design of<br>nanomaterials for applications to<br>Hydrogen storage and electronic<br>devices |
| 26-Sep | Kee Joo Chang<br>(Korea Advanced Institute Of Science<br>and Technology, Professor)                                             | Electronic and transport properties<br>of nanoscale devices based on<br>nanotubes                                                      |
| 28-Sep | Takeshi Sassa<br>(Yamagata University, Professor<br>Emeritus)                                                                   | Studies on Fusicoccane<br>Diterpenoids                                                                                                 |
| 28-Sep | Shigeki Imai<br>(Systems Engineering Laboratories,<br>Corporate Research and Development<br>Group, Sharp Corporation, Director) | Device application of<br>polycrystalline silicon thin film:<br>Fundamental of liquid crystalline<br>process                            |
| 3-Oct  | Helmut Mehrer<br>(Institut für Materialphysik, Universität<br>Münster, Professor)                                               | Diffusion in metals and<br>intermetallics                                                                                              |
| 5-Oct  | Daniele Marre<br>(LAMIA, Genova University, Assistant<br>Professor)                                                             | Recent Developments of research<br>on oxides at LAMIA and<br>COHERENTIA laboratories.                                                  |
| 5-Oct  | Fabio Granozio Miletto<br>(COHERENTIA, NAPOLE<br>UNIVERSITY, Doctor)                                                            | Recent Developments of research<br>on oxides at LAMIA and<br>COHERENTIA laboratories.                                                  |

|        |                                                                                                                           |                                                                                                                             |
|--------|---------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|
| 15-Oct | Asokendu Mozumder<br>(The Notre Dame Radiation Laboratory, Professor Emeritus)                                            | Some Recent Advances in Theoretical Radiation Chemistry                                                                     |
| 22-Oct | Dirk Bold<br>(Department of structural biology, Vrije Universiteit Amsterdam , Associate Professor)                       | Regulation mechanism of F1-ATPase                                                                                           |
| 23-Oct | Peter Bury<br>(Faculty of Electrical Engineering, University of Zilina, Professor)                                        | Acoustoelectric interactions in semiconductor interfaces                                                                    |
| 23-Oct | Qi-Lin Zhou(Nankai University, Professor)                                                                                 | Catalytic enantioselective synthesis of biologically important compounds                                                    |
| 26-Oct | Shigeki Imai<br>(Systems Engineering Laboratories, Corporate Research and Development Group, Sharp Corporation, Director) | Device application of polycrystalline silicon thin film: Fundamental of liquid crystalline process                          |
| 2-Nov  | Robert A Crowell<br>(Brookhaven National Laboratory, Group Leader)                                                        | Fundamental Processes of Ionizing Radiation in the Condensed Phase                                                          |
| 10-Nov | Ortwin Brede<br>(University of Leipzig, Professor)                                                                        | Femtosecond events in the bimolecular free electron transfer                                                                |
| 27-Nov | Pradeep K. Pujari<br>(Bhabha Atomic Research Centre,Scientific Officer H)                                                 | Positron annihilation study of freezing of liquid confined in nanodomains                                                   |
| 28-Nov | Tatsuya Nishino<br>(Department of Biochemistry, University of Oxford,Research fellow)                                     | Function and struture of yeast cohesin                                                                                      |
| 29-Nov | Seidel, Claus A. M.<br>(Heinrich-Heine-Universitaet Dueddeldorf, Professor)                                               | Photochemical Aspects of Single-Molecule Angstroem Optics                                                                   |
| 8-Dec  | H. Ronald Kaback<br>(University of California, Los Angeles, Professor)                                                    | Structure and Mechanism of the Lactose Permease, an Ion-Coupled Membrane Transport Protein                                  |
| 10-Dec | Robert H. Edwards<br>(University of California, San Francisco, Professor)                                                 | The Regulation of Neurotransmitter Transport into Secretory Vesicles                                                        |
| 21-Dec | Shigeki Imai<br>(Systems Engineering Laboratories, Corporate Research and Development Group, Sharp Corporation, Director) | Device application of polycrystalline silicon thin film: Fundamental and application of polycrystalline silicon TFT process |
| 28-Dec | Ramasamy RAMARAJ<br>(Madurai Kamaraj University, India , Professor)                                                       | Nanomaterials for Electrocatalysis and Photocatalysis                                                                       |

|        |                                                                                                                           |                                                                                                                                                  |
|--------|---------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| 21-Jan | Vladimir Kren<br>(Academy of Sciences of the Czech Republic, Professor)                                                   | Silybin and Silymarin in Cancer Prevention ... and Treatment?                                                                                    |
| 21-Jan | Seiji Koide<br>(IHI Corporation, Senior Consulting Manager)                                                               | Theory of Semantic Web, Semantics for RDF(S) and OWL.                                                                                            |
| 22-Jan | Michael George<br>(Nottingham University, GB, Professor)                                                                  | Photochemical Aspects by Time-resolved Infrared Spectroscopy                                                                                     |
| 1-Feb  | Masato Sagawa<br>(Intermetallics Co., Ltd., Representative executive)                                                     | Development of Neodymium magnets in Japan                                                                                                        |
| 6-Feb  | Shigeki Imai<br>(Systems Engineering Laboratories, Corporate Research and Development Group, Sharp Corporation, Director) | Improvement in quality of polycrystalline silicon thin films and improvement in device performance                                               |
| 6-Feb  | David G. Whitten<br>(New Mexico University, USA, Professor)                                                               | Fluorescence detection of functionalized copolymers applied to biological diagnostics                                                            |
| 6-Feb  | Peter Lu<br>(Bowling Green State University, USA, Professor)                                                              | Single Molecule Science of Biological Aspects                                                                                                    |
| 7-Feb  | Arno Schindlmayr<br>(Institute of Solid State Research, Forschungszentrum Juelich, Researcher)                            | Electronic Excitations and Theoretical Spectroscopy                                                                                              |
| 20-Feb | Takayuki Ariga<br>(Department of Science, Kyoto University, Researcher)                                                   | Single molecule study on chimera F1                                                                                                              |
| 25-Feb | Nicola Guarino<br>(ISTC-CNR, Laboratory for Applied Ontology, Professor)                                                  | An Introduction to Formal Ontology                                                                                                               |
| 7-Mar  | Kiyomichi Nakai<br>(Ehime University, Professor)                                                                          | Effects of Phase Transformation on Mechanical Properties of Structural Materials and Radiation-Induced Phase Transformation in Nuclear Materials |
| 10-Mar | Steven Kraines<br>(Department of Chemical System Engineering, Tokyo University, Associate Professor)                      | Mining for semantic patterns in the JST Failure Knowledge Database<br>Steven Kraines                                                             |
| 14-Mar | Sylvain Darses<br>(ENSCP, Paris, France, Maitre de conference )                                                           | Potassium organotrifluoroborates: new perspectives in organic chemistry                                                                          |



|        |                                                                                      |                                              |
|--------|--------------------------------------------------------------------------------------|----------------------------------------------|
| 14-Mar | Jyunji Urakawa<br>(High Energy Accelerator Research<br>Organization(KEK), Professor) | Development of S-band<br>photocathode RF gun |
|--------|--------------------------------------------------------------------------------------|----------------------------------------------|

## 7) Public Information Activity

Public information activity of ISIR in 2007 is as follows:

- Bulletin of ISIR (2007 (in both Japanese and English))
- Memoirs of the Institute of Scientific and Industrial Research,  
Osaka University (Vol.64 2007 (in English))
- Annual Report of ISIR (2007 (in Japanese))
- SANKEN News Letters, 31-33(in Japanese)
- Report on SANKEN TECHNO SALON (2007 (in Japanese))
- WWW home-page (<http://www.sanken.osaka-u.ac.jp/>)  
(English version is available.)

## 8) Research Reports

The number of scientific and technological papers published in 2007 is 467.  
The details are described in the part of activity of divisions and facilities.

## 9) Scientific Awards

|                                               |                                                                                                                                                                                    |
|-----------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| A.HIRATA<br>Y.HIROTSU                         | Metallic Glass Symposium Best Poster Award<br>(Japan Science and Technology Agency)                                                                                                |
| M.ISHIMARU<br>Y.HIROTSU etc.                  | 2007 MRS Fall Meeting Best Poster Award<br>(Materials Research Society)                                                                                                            |
| H.NAKAJIMA                                    | Prizes for Science and Technology -Research Category-<br>(The Commendation for Science and Technology by the<br>Minister of Education, Culture, Sports, Science and<br>Technology) |
| J.S.PARK<br>H.S.KEUN<br>S.SUZUK<br>H.NAKAJIMA | Best poster award at 5th Symposium on the 21st Century COE<br>Program<br>(Project: Center of Excellence for Advanced Structural and<br>Functional Materials Design)                |
| M.TANE<br>H.NAKAJIMA                          | Best poster award at 5th Symposium on the 21st Century COE<br>Program<br>(Project: Center of Excellence for Advanced Structural and<br>Functional Materials Design)                |

|                                     |                                                                                                                                          |
|-------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|
| H.SEKI etc.                         | Best Poster Award<br>(Kansai Branch Meeting of The Japan Institute of Light Metals)                                                      |
| T.MAJIMA<br>T.TACHIKAWA<br>K.NAITO  | Best Poster Award<br>(9th International Symposium on Eco-Materials)                                                                      |
| T.MAJIMA                            | Molecular Science Forum Lecture Professorship<br>(Chinese Chemical Society)                                                              |
| H.SASAI                             | Tetrahedron Letters Most Cited Paper 2004-2007 Award                                                                                     |
| S.TAKIZAWA                          | TETRAHEDRON:ASYMMETRY-Most Downloaded Papers,<br>2006                                                                                    |
| Y.HAYASHI                           | JSiSE Incentive Award<br>(the 32nd Annual Conference of JSiSE)                                                                           |
| Y.MUKAIGAWA                         | Merit Award for Activities in Information and Systems Society<br>(The Institute of Electronics, Information and Communication Engineers) |
| Y.MAKIHARA                          | Yamashita Memorial Research Award<br>(Information Processing Society of Japan)                                                           |
| H.AZUMA                             | Excellent Paper Award in Bachelor Thesis Session<br>(Information Processing Society of Japan, SIG Computer Vision and Image Media)       |
| M.NUMAO                             | The Okawa Publications Prize<br>(The Okawa Foundation for Information and Telecommunications)                                            |
| S.KURIHARA etc.                     | Forum on Information Technology 2007 (FIT2007) Paper Award                                                                               |
| M.NUMAO<br>S.KURIHARA<br>K.MORIYAMA | Technical Stream Best 6 papers<br>(AI-2007 Twenty-seventh SGAI International Conference on Artificial Intelligence)                      |
| S.HONDA                             | Technological encouragement award<br>(Technical Division of Measurement, SICE)                                                           |
| T.WASHIO                            | Excellent Paper Award of Special Interest Group Meeting in<br>The Japanese Society for Artificial Intelligence                           |
| T.WASHIO                            | A fine work in Marketing Analysis Contest<br>(Marketing Analysis Contest, 2007)                                                          |
| K.TAKABAYASHI                       | Student Encouragement Award of Special Interest Group<br>Meeting on Database Systems in Information Processing Society of Japan          |
| Y.SASAKI                            | Best poster award<br>(The 23rd Japan Society of Drug Delivery System)                                                                    |
| H.IMAMURA                           | Early Research in Biophysics Award                                                                                                       |

|                       |                                                                                                                                                          |
|-----------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| S.MURAKAMI            | The Young Scientists' Prize<br>(The Commendation for Science and Technology by the<br>Minister of Education, Culture, Sports, Science and<br>Technology) |
| S.MURAKAMI            | Japan Bio-venture Award<br>(FujiSankei Business i)                                                                                                       |
| K.NISHINO             | Japan Antibiotics Research Association Award<br>(Japan Antibiotics Research Association)                                                                 |
| J.YANG                | Nishikawa Award<br>(Foundation for High Energy Accelerator Science)                                                                                      |
| M.TANIGUCHI           | Young Best Presenter Award<br>(Soceity of Nano Science and Technology)                                                                                   |
| M.TANIGUCHI           | The Award for the Young Distinguished Scientist of the Japan<br>Society for Molecular Science<br>(Japan Society for Molecular Science)                   |
| K.SYOUJI              | Best poster award<br>(Japan Society for Molecular Science)                                                                                               |
| T.KONDO<br>A.ASANO.   | Best poster award at 50th Annual Meeting of Japanese Society<br>of Radiation Chemistry                                                                   |
| K.SUGANUMA<br>K.S.KIM | MES2006 Best Paper Award<br>(Japan Institute of Electronics Packaging)<br>(Prevention of Sn whisker formation by thin Ni film coating)                   |
| K.SUGANUMA            | MES2006 Best Paper Award<br>(Japan Institute of Electronics Packaging)<br>(A study on Pb-free solder electromigration in micro-joint<br>system)          |

## 2. Education

ISIR accepts graduate students (about 220) from the Graduate Schools of Science, Engineering, Engineering Science, Pharmaceutical Science, Information Science and Technology, and Frontier Biosciences, and also researchers for special training, including those from industry and from abroad.

Staff members also belong to various Faculties: Faculty of Science, Faculty of Engineering, Faculty of Engineering Science, Faculty of Pharmaceutical Science, Faculty of Information Science and Technology, and Faculty of Frontier Biosciences. Some members belong to two Faculties. They give lectures for graduate and undergraduate students in each Faculty.

Number of graduate students as of March 31, 2007 is as follows.

| G.S.<br>Course | Science | Engineering | Engineering<br>Science | Pharmaceutical<br>Science | Information<br>Science and<br>Technology | Frontier<br>Biosciences | Total |
|----------------|---------|-------------|------------------------|---------------------------|------------------------------------------|-------------------------|-------|
| Master Course  | 47      | 53          | 18                     | 5                         | 10                                       | 11                      | 144   |
| Doctor Course  | 21      | 38          | 8                      | 6                         | 13                                       | 5                       | 91    |
| Total          | 68      | 91          | 26                     | 11                        | 23                                       | 16                      | 235   |

Number of students who had obtained Master's or Doctor's Degree in 2007 is as follows.

| Field<br>Degree | Science | Engineering | Engineering<br>Science | Pharmaceutical<br>Science | Information<br>Science and<br>Technology | Frontier<br>Biosciences | Total |
|-----------------|---------|-------------|------------------------|---------------------------|------------------------------------------|-------------------------|-------|
| Master Degree   | 17      | 34          | 3                      | 4                         | 7                                        | 1                       | 66    |
| Doctor Degree   | 4       | 14          | 0                      | 2                         | 0                                        | 0                       | 20    |
| Total           | 21      | 48          | 3                      | 6                         | 7                                        | 1                       | 86    |

### 3. International Exchange

#### 1) Exchange Agreement

Academic Exchange Agreements are now concluded with the following 16 organizations.

- Faculty of Natural Science, Otto-von-Gueriche University Magdeburg (Germany)
- College of natural Science, Chungnam National University (Korea)
- Forschungszentrum Jülich GmbH (Germany)
- University of Maryland at COLLEGE PARK (U.S.A.)
- University College London (U.K.)
- College of Natural Sciences, Pusan National University (Korea)
- Research Institute of Industrial Science, Hanyang University (Korea)
- College of Science, National Taiwan University (Taiwan)
- Pacific Northwest National Laboratory (U.S.A.)
- Centre National de la Recherche scientifique : CNRS (France)
- Rwth Aachen University (Germany)
- College of Engineering, Gyeongsang National University (Korea)
- College of Natural Science, Chungnam National University (Korea)
- Institute of Remote Sensing and Geographical Information System, Peking University (China)

- College of Science, National Taiwan Normal University (Taiwan)
- Faculty of Science, University of Geneva(Switzerland)

## **2) Foreign Researchers and Students**

Number of foreign researchers and students staying in ISIR as of March 31, 2008 is 57 in total. Details are, Research Associates (6), Visiting Researchers (1), Part-time Employee (21), Graduate Students (Doctor Course) (19), (Master Course) (10). Their nationalities are: Korea(20), China(16), India/(6), Viet Nam(5), U.K(1), Hungary(1), Russia(1), Brazil(2), Bangladesh(1), Indonesia(1), Philippines(1), Venezuela(1), Egypt(1).

Foreign visitors in 2007 are as follows:

U.S.A. (9), Korea (38), U.K. (3), Germany (6), France(1), Canada (1), India (3), Slovak Republic(4), Czech Republic(1), Finland(1) Total (67).

## **3) International Conferences and Symposiums**

Number of presentations (plenary, invited, oral and poster in various international conferences and symposia) by staff of ISIR is 491 in total.

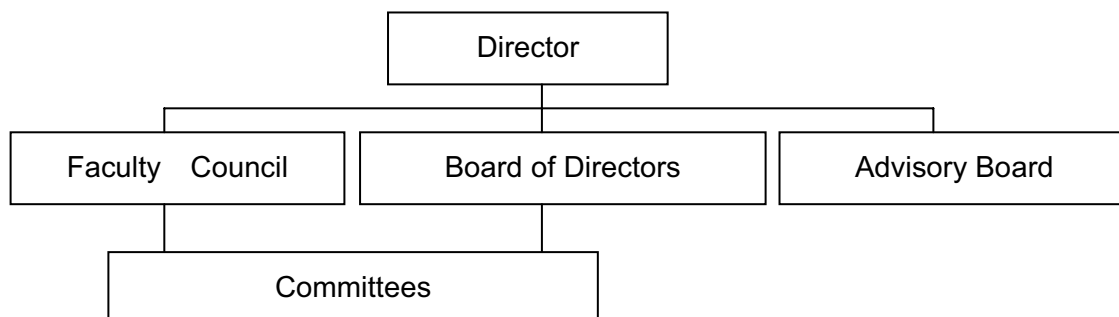
Number of ISIR staffs who have been working as committee members of International Conferences or Editorial Board of international academic journals are 176 in total. For more details, see the part of activity of divisions and facilities.

## **4. Concluding Remarks**

### **(1) Organization and Management System**

At present (March.2008), ISIR has 7 divisions including 28 departments and 3 research Centers, "Nanoscience and Nanotechnology Center" , "Materials Analysis Center" and "Materials Science & Technology Research Center for Industrial Creation". In April 2006, Academia Industry Relation Office (AIR-Office) has been settled in order to strengthen cooperation between the Institute and Industries. In the Institute, brilliant staff together from wide-range fields, professors, associate professors and research associates do research and have scientific communication among scientists. All professors are participant in management system, a Board of Directors under the Director has been formed, and Advisory Board has been set up to introduce opinions from outside into the Institute.

### 【Organization of ISIR】



### (2) Research Activities

For development of industry, researchers of ISIR are exploiting new and interdisciplinary research through basic science and technology

In 1997, Harmonized Materials Research Group was designated as one of the Centers of Excellence (COE) of Ministry of Education, indicating the high research activity of the Institute.

In 2005, Materials Science & Technology Research Center for Industrial Creation has launched as a joint Center between ISIR and Institute of Multidisciplinary Research for Advanced Materials, Tohoku University.

ISIR's research environment as facilities and equipments has been becoming better. A new building was constructed in 2001 and 2003 to the increased number of scientists and the development of Nanotechnology, respectively and Nanoscience and Nanotechnology Center started in April 2002. In addition, the old first research building will be reconstructed from autumn, 2007.

### (3) Education

Considering objective of ISIR, supporting the graduate and undergraduate education is one of the important missions.

The Institute has about 200 graduate students and undergraduate students coming from various departments such as Science and Engineering, and also researchers for special training with "Nano Science".

The Sanken Techno-Salon is one of forums to exchange information between our staff member and the people from industries specializing in electronics, organic chemicals, semiconductors, drugs, etc. We have also seminars for providing seeds of new technologies to the industrial communities. The Institute aim to grow researchers and students with the best humanity, capable of innovating their specific fields of

research from basic point of view.

#### **(4) Contribution to Societies**

As the fast-paced advancement of science and technology and the rapid alteration of social and industrial structures, we must further recognize as the Institute open to society and industry. We consistently strive to deepen our cooperation with society through positively opening of facilities, intellectual properties and achievements to meetings (ex. Sanken Techno Salon) and publications. Through them, we will be able to transfer our industrial seeds for new technology and exchange ideas for new materials. They have been highly evaluated that we have done joint researches with other university/industry.

In April 2005, AIR-office (Academia Industry Relations Office) has been settled in order to strengthen cooperation between the Institute and industries.

#### **(5) International Exchange**

International Exchange is one of indispensable element for our Institute. We are trying to open the door widely to invite more researchers and students from other countries, and we have 3 kind of International exchange, Academic Exchange, Student Exchange and branches in France and USA. At present (March, 2008), 57 foreign researchers and students join in the Institute. International Conferences sponsored by our Institute have been held twice a year since 1998. It's so important to release our results towards all over the world and have a chance to exchange opinions with foreign scientists.

#### **(6) Future Plan and Prospect**

In order to respond with flexibility to our quickly changing society, along with the rapid development of science and technology, we must understand our role of society and in order to stay effective and relevant Institute for industries, we must make independent researches and release widely our intellectual properties and achievement.

Keeping development of science and technology in Japan, we must cultivate researchers capable of producing academic and professional results that will benefit the people living on this planet. ISIR grow researchers and students who can active in the world.

You can see about ISIR on the following URL. (<http://www.sanken.osaka-u.ac.jp/>) The Institute of Scientific and Industrial Research keeps making efforts toward higher level contribution to science and industries, and keeps learning.

# **Activities of Divisions**



# Division of Quantum Engineering

## Outline

New, advanced materials and fabrication techniques of nanostructures that allow the realization of the desired quantum effects of electrons, photons and spins are indispensable for the creation of novel electronic, photonic and spintronic devices. The Division of Quantum Engineering is engaged in experimental and theoretical research on these subjects aiming to establish the basis of future electronic/photonic/spintronic devices based on novel quantum effects. The Division of Quantum Engineering is composed of four departments: Quantum Molecular Devices, Photonic and Electronic Materials, Semiconductor Electronics and Condensed Matter Physics. Various approaches are being taken in the fields of electronic materials design and tailoring, surface physics, nanometer scale materials fabrication and characterization, semiconductor nanostructures for quantum devices, semiconductor-based new bio/chemical sensors and computational physics.

Research areas studied and techniques employed by the Division of Quantum Engineering include atomic and electronic structures of semiconductor surfaces and interfaces, nanofabrication processes using scanning probe microscopy, crystal growth of biomolecules, epitaxial growth of compound semiconductors by molecular beam epitaxy, characterization of structural, electric, optical and magnetic properties of semiconductor materials, formation and characterization of low-dimensional semiconductor quantum structures, fabrication of new semiconductor and quantum structure devices, control of the physical properties of carbon nanotubes and the fabrication of single electron transistor, and prediction of new functional materials and fabrication processes design using first principles and electronic structure calculations. Interdisciplinary researches in cooperation with other divisions are also pursued.

## Achievements

- Understanding of the mechanisms of nanostructure relaxation, shape transformation of mesoscopic scale structures, and protein crystallization
- Molecular fluorescence of organic films by STM-induced luminescence spectroscopy
- Crystal growth, characterization and device application of new semiconductors including III-nitride-based ferromagnetic semiconductors, TI-III-V-N, III-nitride nanorod and quantum nanostructures
- Chirality control of carbon nanotube growth
- Carbon nanotube quantum devices
- Integrated carbon nanotube biosensors
- Prediction of new functional materials, high efficient energy conversion materials and fabrication processes by first principles electronic structure calculations
- Materials and device design for semiconductor spintronics from the first principles
- Materials process design and quantum simulation by electronic excitations from the first principles
- Prediction of the electronic structure in organic-metal interface for organic-molecular electronics and materials design from the first principles

## Department of Quantum Molecular Devices

Professor: Hiroshi IWASAKI  
Associate Professor: Koichi SUDOH  
Research Associates: Hongwen LIU, Jun NAKAMURA  
Post Doctoral Fellow: Tiezhu HAN  
Graduate Students: Nobuyasu HORI, Mahito YAMAMOTO  
Under Graduate Students: Masakazu OKANO, Tomohito KASHIWAGI  
Supporting Staff: Kiyomi HIRASAWA

### Outline

The Department of Quantum Molecular Devices is engaged in study of multi-scale surfaces/interfaces structures and nanoscale properties of materials for development of novel devices that integrate the quantum mechanical features of semiconductors and molecular functions of organic- and bio-molecules. In more concrete terms, we are studying dynamics of atomic steps on crystal surfaces with UHV- scanning tunneling microscopy (STM), behaviors of surface/interface structures under non-equilibrium conditions such as crystal growth and phase separation, crystal growth and applications of biomolecules by atomic force microscopy (AFM), physical modeling and simulation of mesoscale structures and luminescent organic films by STM-induced luminescence spectroscopy.

### Current Research Projects

#### Evolution of Nano- and Mesoscopic-scale Structures on Semiconductor Surfaces

Mechanism of morphological evolution of semiconductor surfaces at nano and mesoscopic scales has been studied. Performing real-time observation of Ostwald ripening of two-dimensional islands and decay of nanoscale holes by high temperature scanning tunneling microscopy (STM), the mechanisms of surface mass transport involved in these processes have been revealed. Besides, shape transformation of micron scale holes with high aspect ratios on Si(001) substrates by high temperature hydrogen annealing has been investigated. The detail of the complex evolution of a hole due to surface self-diffusion was presented.

#### Study on Growth Mechanism of Protein Crystals

Crystallization of sweet protein thaumatin has been studied from microscopic viewpoint by in-situ atomic force microscopy (AFM). It has been shown that monovalent cations contained in the protein solution affect the molecular arrangement in the tetragonal thaumatin crystals. Furthermore, individual molecular level processes involved in step advancement on thaumatin (101) surfaces were revealed by AFM.

#### Study of Luminescent Organic Films by STM-induced Luminescence

We investigate scanning tunneling microscope (STM)-excited fluorescence from porphyrin thin films on various combinations of substrates (Pt, Ag, Au and ITO) and

PtIr, Ag and Au tips. We calculate relative electromagnetic-field powers in the tip-substrate gaps, which are in consistent with the observed intensities of the plasmon-mediated light emissions. We find enhancement of STM-excited fluorescence owing to field confinement effect and plasmonic gap modes.

## **Publications**

### **Review Papers**

Nanoscale Control of Silicon Microstructures by High Temperature Hydrogen Annealing, R. Shimizu and H. Iwasaki, OYO BUTURI, vol. 76 No.7 (2007) 764-770.

STM Light Emission Spectroscopy from Organic Films, H. Iwasaki, L. Hongwen, R. Nishitani, J. Surf. Sci. Soc. Jpn. vol. 29, No.1 (2007) 50-54.

### **Books**

Application of Quantum Dots for Life Science Field (part), Hiroshi Iwasaki, CMC Publishing CO. Ltd. (2007).

### **Contributions to International Conferences and Journals**

H. Iwasaki                      JEJU 2007 ISPM (International Scanning Probe Microscopy Conference), Jeju, South Korea, June 10~ 14, 2007  
(Committee member)

### **Publications in Domestic Meetings**

|                                                         |          |
|---------------------------------------------------------|----------|
| The Physical Society of Japan                           | 4 papers |
| The Surface Science Society of Japan                    | 1 paper  |
| The Japanese Association for Crystal Growth Cooperation | 1 paper  |

## **Academic Degrees**

### **Master Degree for Engineering**

|             |                                                                       |
|-------------|-----------------------------------------------------------------------|
| N. Hori     | AFM Study on Effect of Solution Conditions on Protein Crystallization |
| M. Yamamoto | Decay Dynamics of Nanostructures on SrTiO <sub>3</sub> (001)          |

## **Sponsorships**

### **Entrusted Research**

|        |                                     |                                                                                     |            |
|--------|-------------------------------------|-------------------------------------------------------------------------------------|------------|
| H. Liu | Japan Science and Technology Agency | Enhancement of Molecular Fluorescence of Metal Cluster Containing Organic Molecules | ¥2,000,000 |
|--------|-------------------------------------|-------------------------------------------------------------------------------------|------------|

**Other Research Fund**

|            |                                                   |          |
|------------|---------------------------------------------------|----------|
| H. Iwasaki | Fuji Electric<br>Device<br>Technology<br>Co., LTD | ¥500,000 |
|------------|---------------------------------------------------|----------|

## Department of Photonic and Electronic Materials

Professor: Hajime ASAH  
Associate Professor: Shigehiko HASEGAWA  
Assistant Professor: Shuichi EMURA  
Post Doctoral Fellow: Shanthi SUBASHCHANDRAN  
Research Technical Expert: Daivasigamani KRISHNAMURTHY  
Graduate Students: Shigeya KIMURA, Jong-Uk SEO, Keisuke ARAKI  
Motoki OZASA, Hiroyuki TAMBO, Satoko HAYAKAWA  
Yuki HIROMURA, Hisashi KAMEOKA  
Masahiro TAKAHASHI, Yusuke TANAKA  
Katsuhiko TOKUDA, Yuya HONDA  
Research Student: Jin-Qiang LIU, Siti Nooraya MOHD TAWIL  
Support Staff: Akiko WATANABE

### Outline

The department of Photonic and Electronic Materials makes research on materials, mainly semiconductors and related materials, and processing on them. Four steps are required in materials research, that is, materials design, materials synthesis (crystal growth) and processing, materials characterization, and device application. In materials design, study on finding required characteristics by changing the combination and ratio of atoms is conducted. In materials synthesis, study on molecular beam epitaxy growth is mainly carried out, in which the crystal growth is done by supplying molecules and atoms onto the substrate surface. In materials characterization, structure investigation by electron diffraction, X-ray diffraction, STM, EXAFS and Raman scattering, optical characterization by photoluminescence, optical absorption and so on, electrical characterization by Hall measurement, and magnetic characterization by SQUID are carried out. In device application, basic researches on photonic devices such as lasers, electronic devices such as field emission devices, and spintronic devices are conducted.

### Current Research Projects

#### 1. Crystal Growth and Properties of Diluted Magnetic Semiconductors

Diluted magnetic semiconductors, which have two characters of semiconductors and magnetic materials, are gathering interest as a candidate for new functional materials. In 2001, we succeeded in the growth of GaCrN and observed the room temperature ferromagnetism as well as the PL emission. We also observed the room temperature ferromagnetism together with sharp PL emission for the rare-earth doped GaN, GaGdN. In 2005, GaCrN/GaN/GaCrN trilayer structure tunnel diodes were fabricated and tunnel magnetoresistance effect was observed at 77 K. In 2006, successful low temperature (300°C) growth of high Gd concentration (12%) GaGdN with improved ferromagnetism was realized. In 2007, it was found that the co-doping of Si further increases the magnetization. Together with the observation of enhanced magnetization in GaGdN/GaN superlattice structures these results were understood as carrier-induced ferromagnetism. Successful growth of GaCrN and GaGdN nano-rod structures and the observation of room temperature ferromagnetism were also realized.

## **2. Growth, Characterization and Device Application of Semiconductor-Semimetal Mixed Crystals; New Semiconductors Including TI**

In 1995, we proposed new semiconductors TlInGaAs in which the bandgap energy is independent of temperature. We have grown TlInGaAs by MBE and confirmed the small temperature variation of the bandgap energy and refractive index. In 2005, we fabricated the TlInGaAs/TlInP/InP SCH LDs and obtained the small temperature variation of lasing peak wavelength as small as 0.06 nm/K in the relatively wider temperature range. We also proposed the TlInGaAsN/AlGaAs for both temperature-stable wavelength and threshold current LDs. In 2006, we found that the TI incorporation is much improved by the use of TI-contained cladding layers and barrier layers and by the co-doping of nitrogen (N) atoms. In 2007, to solve the PL intensity degradation problem encountered when co-doped with N atoms, the layer structures and the growth conditions were intensively studied and the comparable PL intensities without post-growth thermal annealing were obtained.

## **3. Growth of GaN Nano-Rods and Application to Field Emitter**

III-V nitride semiconductors gather much interest from the viewpoint of application to light emitting devices as well as devices used in harsh environment. We have observed the strong PL emission from the grown polycrystalline GaN and proposed the wide variety of device applications. We also obtained the good electric field emission (FE) characteristics of electrons from GaN/metal samples, which is promising to fabricate the FE electron source devices. We also formed the GaN nano-rod structures on Si substrate and obtained the very small threshold voltage of 1.1 V/ $\mu\text{m}$  for the FE. In 2007, the growth condition dependencies of GaN nano-rod structural properties and their relation to the FE characteristics were studied and it was found that the size and the gap space of nano-rods are controlled. By changing the gap space the special uniformity of FE was improved.

## **4. Growth of III-V Semiconductors on Sub-Micron Localized Areas of Si Surface**

III-V semiconductors are attracting considerable attention as channel materials in the future advanced MISFETs with high performance (Beyond Si-CMOS), owing to their high electron mobility. To accomplish this, the formation of III-V-on-Insulator (III-V-O-I) on Si is mandatory. In 2007, the selective MBE growth of InP on sub-micron localized areas of Si substrate was successfully realized.

## **5. Spin Injection into Diluted Magnetic Semiconductors from Magnetic Metals and Their Nano-Magnetic Properties**

Spin injection behavior from magnetic metals into diluted magnetic semiconductors (DMSs) is very important to realize semiconductor spintronics devices in addition to operate spin polarized scanning tunneling microscopy (STM) to DMSs. In 2007, as a first step, Fe metals were grown on GaN and their crystal structures, growth mode and magnetic properties were intensively studied. It was found that magnetic characteristics greatly depend on the amount of deposited Fe metals and their structures.

## **6. Nano-Observation and Characterization of Short-Channel MOSFET**

The nano-structural and physical properties of short-channel MOSFETs have been

studied with STM. We have conducted the STM observation on transverse and longitudinal cross-sections of short-channel MOSFETs and succeeded in the nano-scale characterization of the source/drain structures as well as the fluctuation of the gate along the channel-width direction. The computer simulation of 3-dimensional potential profiles in short-channel MOSFETs with transverse and tilted cross-sections agreed well with the experimental observations. In 2007, the relaxation process of electrons and holes injected from the STM tip into the p-n junction area of MOSFET and their transport routes were studied and made clear.

## **7. XAFS Characterization of New Functional Materials**

XAFS is spectroscopy-based new characterization technique for analyzing atomic scale structures of materials and is only one technique directly analyzing the atomic arrangements/coordination for amorphous materials as well as very low density elements in materials. The atomic arrangements/coordination in new functional materials, GaCrN and GaGdN, was characterized and it was showed that the Cr (Gd) atoms substitutionally occupy group III sites. We also found the possibility of the shift of Cr atoms from the tetrahedron center in GaCrN, which was considered to strongly affect the ferromagnetism of GaCrN. It was shown that the Cr atoms substitutionally occupy group III sites in the GaCrN nano-rods grown at reduced temperatures.

## **Publications**

### **Original Papers**

Cr atom alignment in Cr-delta-doped GaN, S. Kimura, S. Emura, H. Ofuchi, Y. Nakata, Y.K. Zhou, C.W. Choi, Y. Yamauchi, S. Hasegawa and H. Asahi: American Institute of Physics, CP 882 (2007) 410-412.

MBE growth of TlInGaAs/TlInP/InP SCH LD structures and their laser operation with low temperature variation of lasing wavelength, A. Fujiwara, D. Krishnamurthy, T. Matsumoto, S. Hasegawa and H. Asahi: J. Cryst. Growth, 301-302 (2007) 109-112.

Growth and Characterization of Ferromagnetic Cubic GaCrN: Structural and magnetic properties, S. Kimura, S. Emura, H. Ofuchi, Y. Zhou, S. Hasegawa and H. Asahi: J. Cryst. Growth, 301-302 (2007) 651-655.

TlGaInNAs/GaAs Double Quantum Well Structures: Effect of Barrier Layers and Substrate Orientation, D. Krishnamurthy, T. Matsumoto, A. Fujiwara, S. Hasegawa and H. Asahi: J. Cryst. Growth, 301-302 (2007) 534-538.

Observation of Valence State Change in Layered  $\text{Li}_{1-y}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ , Hironori Kobayashi, Yoshinori Arachi, Shuichi Emura, K. Handa, K. Tatsumi: AIP Conference Proceedings Volume, 882 (2007) 478 - 480.

Alternation of the Pd Lattice in Nano-Sized-Pd/ZrO<sub>2</sub> Composite during Hydrogen Absorption, Yoshinori Arachi, Shuichi Emura, Akira Omura, Masanobu Nunogaki, Takeshi Asai, Shinichi Yamaura, Akishisa Inoue, Yoshiaki Arata: AIP Conference Proceedings Volume, 882 (2007) 740-742.

Formation process of sharp-pointed structures on GaN nanorods during RF-MBE growth and their field emission characteristics, M. Terayama, S. Hasegawa, K. Uchida, M. Ishimaru, Y. Hirotsu and H. Asahi: Phys. Stat. Sol. (c), 4 (7) (2007) 2371-2374.

Quinary TlGaInNAs DQW Structures: Effect of Growth Temperature and Growth Rate on Tl Incorporation, D. Krishnamurthy, A. Fujiwara, S. Hasegawa and H. Asahi: Proc. 19th Int. Conf. on InP and Related Materials, (2007) 327-330.

Molecular-beam epitaxy growth and characterization of ferromagnetic cubic GaCrN on GaAs substrate, S. Kobayashi, S. Shanthi, S. Kimura, Y.K. Zhou, S. Emura, S. Hasegawa and H. Asahi: J. Cryst. Growth, 308 (1) (2007) 58-62.

Surface modification of a metal into a thick ceramic layer and a model for analyzing the increased hardness, S. Emura, M. Nunogaki and Y. Nakata: J. Ceramic Processing Research, 8 (3) (2007) 191-194.

High Gd concentration GaGdN grown at low temperatures, Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi: Journal of Superconductivity and Novel Magnetism, 20 (6) (2007) 429-432.

### **Review Papers**

Synthesis of Semiconductor Nanospintronics Materials, S. Hasegawa, Y.K. Zhou and H. Asahi, Future Materials 7(4) (2007) 34-39 (in Japanese).

### **Books**

Effectiveness of XAFS method in the study of catalyst materials – Analysis of adsorption behavior of nitrogen molecules on CuZSM-5 at room temperature, Y. Kuroda and S. Emura: in *Development of Advanced Catalyst by using High Brightness Synchrotron Radiation Light at Spring-8* (2007) 201-215 (in Japanese).

### **Patents**

### **International Conferences**

Quinary TlGaInNAs based Heterostructures: Properties and Challenges (INVITED) (invited), D. Krishnamurthy, A. Fujiwara, M. Ozasa, K. Araki, S. Hasegawa and H. Asahi: The 2nd Japan-India Workshop on Optoelectronic Materials and Devices based on Micro to Nano-technology.

Quinary TlGaInNAs DQW Structures: Effect of Growth Temperature and Growth Rate on Tl Incorporation, D. Krishnamurthy (poster), A. Fujiwara, M. Ozasa, K. Araki, S. Hasegawa and H. Asahi: 19th International Conference on Indium Phosphide and Related Materials (IPRM2007).

MBE Growth and Characterization of Rare-Earth Doped Nitride Semiconductors for Spintronics (INVITED) (invited), H. Asahi, Y.K. Zhou, S. Emura and S. Hasegawa: E-



MRS2007.

High Gd concentration GaGdN grown at low temperature (poster), Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi: SpinTech-IV.

Enhancement of magnetic moment in GaGdN/GaN superlattice structure (poster), Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi: ChinaNANO 2007.

Enhancement of magnetic moment in GaGdN/GaN superlattice structure, Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi: Material Today Asia.

Growth and characterization of InCrN and (In,Ga,Cr)N diluted magnetic semiconductors (poster), S. Kimura, S. Emura, Y. Hiromura, Y.K. Zhou, S. Hasegawa and H. Asahi: 7th International Conference on Nitride Semiconductors.

Fabrication and analysis of GaN nanorods on the patterned SOI substrate by MBE (poster), J.U. Seo, S. Hasegawa, and H. Asahi: 34th International Symposium on Compound Semiconductors.

Selective growth of InP on localized areas of silicon (100) substrate by molecular beam epitaxy (poster), K. Araki, S. Hasegawa and H. Asahi: 34th International Symposium on Compound Semiconductors.

Visualization of current pathways in depleted regions of Si pn junctions under scanning tunneling microscope observation (poster), S. Hasegawa: 9th International Conference on Atomically Controlled Surfaces.

TlInGaAsN Novel Semiconductors and Temperature-Stable Lasing Wavelength Laser Diodes (INVITED) (invited), H. Asahi, S. Hasegawa, A. Fujiwara and D. Krishnamurthy: 2008 SPIE Photonics West Conference.

Selective Growth of InP on Patterned Si(001) Substrates by Molecular Beam Epitaxy (poster), S. Hasegawa, K. Araki, J.-U. Seo, and H. Asahi: 11th SANKEN International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium.

Deformation of CrN<sub>4</sub> tetrahedron site symmetry in GaCrN detected by X-ray linear dichroism (poster), S. Emura, S. Kimura, H. Tambo, Y. Hiromura, Y.K. Zhou, S. Hasegawa and H. Asahi: 11th SANKEN International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium.

Enhancement of magnetic properties in GaGdN/GaN superlattice structure and low-temperature-grown GaGdN layer (poster), Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi: 11th SANKEN International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium.

#### **Contributions to International Conferences and Journals**

H. Asahi      2007 International Conference on Solid State Devices and Materials (Program

|             |                                                                                                                                                   |
|-------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
|             | Committee member)                                                                                                                                 |
| H. Asahi    | 19th International Conference on Indium Phosphide and Related Materials<br>(Organizing Committee member, International Steering Committee member) |
| H. Asahi    | International Symposium on Compound Semiconductors 2007<br>(Organizing Committee member, Program Committee member)                                |
| H. Asahi    | 4th Vacuum and Surface Science Conference of Asia and Australia (Program<br>Committee member)                                                     |
| H. Asahi    | 2008 International Conference on Solid State Devices and Materials (Program<br>Committee member)                                                  |
| H. Asahi    | 15th International Colloquium on Scanning Probe Microscopy (Publication<br>Committee member)                                                      |
| H. Asahi    | 20th International Conference on Indium Phosphide and Related Materials<br>(International Steering Committee member)                              |
| H. Asahi    | 15th International Conference on Molecular Beam Epitaxy (International<br>Advisory Committee member)                                              |
| H. Asahi    | Second International Symposium on Growth of III-Nitrides (International<br>Advisory Committee member)                                             |
| H. Asahi    | Journal of Crystal Growth (Editor)                                                                                                                |
| H. Asahi    | Current Applied Physics (Editorial Board member)                                                                                                  |
| H. Asahi    | J. Materials Science: Materials in Electronics (Editorial Board member)                                                                           |
| H. Asahi    | Journal of Ceramic Processing Research (Editor)                                                                                                   |
| H. Asahi    | Journal of Physics: Condensed Matter (Advisory Editorial Board member)                                                                            |
| H. Asahi    | e-Journal of Surface Science and Nanotechnology (Advisory Board member)                                                                           |
| S. Hasegawa | 19th International Conference on Indium Phosphide and Related Materials<br>(Local Arrangements Committee member)                                  |
| S. Hasegawa | Second International Symposium on Growth of III-Nitrides (Financial Committee<br>member)                                                          |

### **Publications in Domestic Meetings**

|                                                                       |           |
|-----------------------------------------------------------------------|-----------|
| The Japan Society of Applied Physics                                  | 17 papers |
| PASPS Symposium                                                       | 6 papers  |
| Electronic Materials Symposium                                        | 2 papers  |
| The Institute of Electronics, Information and Communication Engineers | 1 paper   |

### **Academic Degrees**

#### **Master Degree of Engineering**

|             |                                                                                         |
|-------------|-----------------------------------------------------------------------------------------|
| M. Ozasa    | Study on Growth and Characterization of TlInGaAs(N) on InP substrates                   |
| H. Tambo    | Study on Formation and Characterization of GaCrN Vertical Nanostructures                |
| Y. Hiromura | Study on Crystal Growth and Characterization of Diluted Magnetic<br>Semiconductor GaGdN |

#### **Master Degree of Science**

|          |                                                                   |
|----------|-------------------------------------------------------------------|
| K. Araki | Selective Growth of InP on Localized Areas of Si (100) substrates |
|----------|-------------------------------------------------------------------|

S. Hayakawa      Formation of Fe dots on GaN and Characterization of their Structural and Magnetic Properties

**Doctor Degree of Engineering**

S. Kimura      Study on Synthesis of III-Nitride Diluted Magnetic Semiconductors and their Physical Properties

**Sponsorships**

**Grant-in-Aid for Scientific Research (B) (2)**

H. Asahi      Study on Room Temperature Ferromagnetic Nitride Semiconductor Nanostructures and Application to Nanospintronics Devices      ¥5,500,000

**Grant-in-Aid for Scientific Research on Priority Areas**

H. Asahi      Study on Fabrication of InN-Based Long Wavelength Circular Polarized Semiconductor Lasers      ¥3,700,000

**Grant-in-Aid for Creative Scientific Research**

H. Asahi      Development of properties and functionalities by precise control of rare-earth doping (Y. Fujiwara)      ¥30,420,000

**Entrusted Research**

J.U. Seo      Marubun Research Study on Fabrication of GaN      ¥1,500,000  
Promotion      Nanorods and their Electric Field  
Foundation      Emission Characteristics

## Department of Semiconductor Electronics

|                          |                                                                                                                                      |
|--------------------------|--------------------------------------------------------------------------------------------------------------------------------------|
| Professor:               | Kazuhiko MATSUMOTO                                                                                                                   |
| Associate Professor:     | Koichi INOUE                                                                                                                         |
| Assistant Professor:     | Kenzo MAEHASHI, Yasuhide OHNO                                                                                                        |
| Post Doctoral Fellows:   | Takafumi KAMIMURA                                                                                                                    |
| Graduate Students:       | Hideo NAGAHAMA, Yasuki YAMAMOTO,<br>Yoshihiro ASAI, Taiji KATSURA, Kohei NISHIGUCHI,<br>Shin IWASAKI, Yuichi TSUJITA, Satoshi NAGASO |
| Under Graduate Students: | Tomoki TSUJI, Takaomi KISHIMOTO                                                                                                      |
| Supporting Staff:        | Saori KONO                                                                                                                           |

### Outline

Semiconductors quantum structures, where electrons and photons play remarkable roles owing to quantum effects, are expected to show superior properties. We study the basic problems in the fabrication and the characterization of such quantum structures in the atomic scale. The research activities include applications to new devices based on the quantum effects with the coherent ballistic transport of carriers and electron-photon interactions.

Carbon nanotubes (CNTs), especially single-walled carbon nanotubes (SWNTs), are a promising material to realize quantum-effect devices because of their unique nano-structures. As a sensor of single charge or spin with the high sensitivity, the formation and characterization of field-effect transistors (FETs) and single electron devices using carbon nanotubes are studied using thermal CVD method, Raman scattering spectroscopy, scanning probe microscopy, and photoluminescence spectroscopy.

### Current Research Programs

#### **Resonant Raman scattering study of SWNTs under the irradiation of infrared laser**

Semiconducting SWNTs are gradually decreased in the atmosphere by the infrared (IR) pulse-laser light irradiation in the region of the excitation between the second valence and conduction bands in the SWMTs. We studied the process by Raman scattering spectra in the resonant condition between the third valence and conduction bands, simultaneously using visible Ar ion laser light. The threshold IR powers, the reduction ratios, and the reduction rates in the processes have been clarified.

#### **Carbon nanotube single-electron transistors fabricated by defect-induced plasma process**

We propose and demonstrate the "defect-induced plasma process" for the fabrication of the room-temperature-operated carbon nanotube single-electron transistors (CNT-SETs) with the SiO<sub>2</sub> protection films on the CNT channels. After introducing of defects in the CNT channels by O<sub>2</sub> plasma irradiation through the SiO<sub>2</sub> protection films, multi-quantum dots were fabricated in the CNT channels. The electrical properties of

the CNT-SETs suggested that the oscillation in the drain currents as a function of the gate voltage was observed at room temperature, as a result of the Coulomb blockade effect. The results indicate that the high yield of the CNT-SETs is as high as approximately 35%. Consequently, the defect-induced plasma process is useful for obtaining the high yield efficiency of CNT-SETs operating at room temperature.

#### **Fabrication of amperometric biosensors based on carbon nanotube-arrayed electrodes**

We fabricated carbon nanotube (CNT) amperometric chips with pneumatic micropumps by the combination of amperometric biosensors based on CNT-arrayed electrodes and microchannels with pneumatic micropumps. Our chip can automatically exchange reagents on the CNT electrodes and clearly detect molecules. Moreover, by modifying the CNT electrodes with enzyme glucose oxidase, glucose molecules could be detected using our chips by cyclic voltammetry and chronoamperometry. We conclude that microfluidic chips with CNT-arrayed electrodes are a promising candidate for the development of hand-held electrochemical biosensors.

#### **Publications**

##### **Original Papers**

Growth of Suspended Single-Walled Carbon Nanotubes by Laser-Irradiated Chemical Vapor Deposition, Y. Asai, Y. Fujiwara, Y. Ohno, K. Maehashi, K. Inoue and K. Matsumoto: J. Physics, 61 (2007) 46-50.

Single-Walled Carbon Nanotube-Arrayed Microelectrode Chip for Electrochemical Analysis., Jun Okuno, Kenzo Maehashi, Kazuhiko Matsumoto, Kagan Kerman, Yuzuru Takamura and Eiichi Tamiya: Electrochem. Commun., 9 (2007) 13-18.

Formation of single quantum dot in single-walled carbon nanotube channel using focused-ion-beam technique, Kenzo Maehashi, Hirokazu Ozaki, Yasuhide Ohno, Koichi Inoue, Kazuhiko Matsumoto, Shu Seki, Seiichi Tagawa: Appl. Phys. Lett., 90 (2007) 023103/1-3.

Label-free protein biosensors based on aptamer-modified carbon nanotube field-effect transistors, Kenzo Maehashi, Taiji Katsura, Kazuhiko Matsumoto, Kagan Kerman, Yuzuru Takamura and Eiichi Tamiya: Anal. Chem., 79 (2007) 782-787.

Label-free immunosensor for prostate-specific antigen based on single-walled carbon nanotube array-modified microelectrodes, Jun Okuno, Kenzo Maehashi, Kazuhiko Matsumoto, Kagan Kerman, Yuzuru Takamura and Eiichi Tamiya: Biosens. Bioelectron., 22 (2007) 2377-2381.

Coulomb Oscillations at Room-Temperature of Single-Walled Carbon Nanotube Field-Effect Transistors, Yasuhide Ohno, Yoshihiro Asai, Kenzo Maehashi, Koichi Inoue and Kazuhiko Matsumoto: Technical Proceeding of the 2007 NSTI

Nanotechnology Conference and Trade Show, 1 (2007) 69-72.

High-sensitive Label-free Biosensors Based on Carbon Nanotube Field-effect Transistors Modified with Aptamers, Kenzo Maehashi, Taiji Katsura, Kazuhiko Matsumoto, Kagan Kerman, Yuzuru Takamura and Eiichi Tamiya: Technical Proceeding of the 2007 NSTI Nanotechnology Conference and Trade Show, 2 (2007) 202-205.

### **International Conferences**

Single Charge Detection Using Single-Walled Carbon Nanotube Single-Hole Transistor, \*Takafumi Kamimura, Yasuhide Ohno, and Kazuhiko Matsumoto: International Semiconductor Device Research Symposium, Maryland, USA, December 12 - 14, 2007.

Coexistence of Coulomb blockade effect and coherent transport of hole in carbon nanotube transistor, \*K. Matsumoto and T. Kamimura: International Symposium on Advanced Nanodevices and Nanotechnology, Hawaii, USA, December 2 - 7, 2007.

Determination method of energy band gap of carbon nanotube by high temperature dependence of current (poster), \*Masatoshi Maeda, Takafumi Kamimura, Shin Iwasaki, Kazuhiko Matsumoto: 17th International Vacuum Congress, 13th International Conference on Surface Science and International Conference on Nano Science and Technology, Stockholm, Sweden, July 2 - 6, 2007.

Magnetoresistance in quantum interference regime of single walled carbon nanotube (poster), \*Takafumi Kamimura, Yasuhide Ohno, Kazuhiko Matsumoto: 17th International Vacuum Congress, 13th International Conference on Surface Science and International Conference on Nano Science and Technology, Stockholm, Sweden, July 2 - 6, 2007.

Single Charge Sensing by Carbon Nanotube Single-Hole Transistor, \*Kazuhiko Matsumoto: AVS 54th International Symposium & Exhibition, Seattle, USA, October 14 - 19, 2007.

Determination Method of Energy Band Gap of Carbon Nanotube (poster), \*Masatoshi Maeda, Takafumi Kamimura, Shin Iwasaki, and Kazuhiko Matsumoto: 2007 International Symposium on Compound Semiconductors, Kyoto, Japan, October 15 - 18, 2007.

Dependence on Top Gate Structure for Sensitivity of Biosensors with Carbon Nanotube Field Effect Transistors (poster), \*Masuhiro Abe, Katsuyuki Murata, Tatsuaki Ataka, and Kazuhiko Matsumoto: 2007 International Symposium on Compound Semiconductors, Kyoto, Japan, October 15 - 18, 2007.

Improvement of Hysteresis Characteristics in Carbon Nanotube Field-Effect Transistors (poster), \*Kohei Nishiguchi, Yasuhide Ohno, Kenzo Maehashi, Koichi Inoue, and Kazuhiko Matsumoto: 2007 International Symposium on Compound Semiconductors, Kyoto, Japan, October 15 - 18, 2007.

Laser-Irradiated Chemical Vapor Deposition for Growth of Single-Walled Carbon Nanotubes (poster), \*Yoshihiro Asai, Yasuyuki Fujiwara, Kenzo Maehashi, Yasuhide Ohno, Koichi Inoue, and Kazuhiko Matsumoto: 2007 International Symposium on Compound Semiconductors, Kyoto, Japan, October 15 - 18, 2007.

High-sensitive Carbon Nanotube Protein Sensors (poster), \*Kenzo Maehashi, Jun Okuno, Taiji Katsura, Kazuhiko Matsumoto, Kagan Kerman, Yuzuru Takamura, and Eiichi Tamiya: 2007 International Symposium on Compound Semiconductors, Kyoto, Japan, October 15 - 18, 2007.

Comparison of Top Gate Structure for Carbon Nanotube Field Effect Transistor Biosensor, \*Masuhiro Abe, Katsuyuki Murata, Tatsuaki Ataka, and Kasuhiko Matsumoto: 2007 International Conference on Solid State Device and Materials, Tsukuba, Japan, September 19 - 21, 2007.

Microfluidic Amperometric Biochips Based on Carbon Nanotube Arrayed Electrodes, \*Yuichi Tsujita, Kenzo Maehashi, Kazuhiko Matsumoto, Hyukchang Kwon, Yuzuru Takamura, and Eiichi Tamiya: 2007 International Conference on Solid State Device and Materials, Tsukuba, Japan, September 19 - 21, 2007.

Single charge sensitivity of single-walled carbon nanotube single-hole transistor, \*Takafumi Kamimura, Yasuhide Ohno, and Kazuhiko Matsumoto: 2007 International Conference on Solid State Device and Materials, Tsukuba, Japan, September 19 - 21, 2007.

New Measurement Method of Carbon Nanotube Energy Band Gap, \*Masatoshi Maeda, Takafumi Kamimura, Shin Iwasaki, and Kazuhiko Matsumoto: 2007 International Conference on Solid State Device and Materials, Tsukuba, Japan, September 19 - 21, 2007.

Characteristics of Carbon Nanotube Field-Effect Transistor Biosensor without Top-Gate Metal Electrode, \*Masuhiro Abe, Katsuyuki Murata, Tatsuaki Ataka and Kazuhiko Matsumoto: 49th Electronic Materials Conference, University of Notre Dame, Indiana, USA, June 20 - 22, 2007.

Determination Method of Energy Band Gap of Carbon Nanotube by High Temperature Dependence of Current, \*Masatoshi Maeda, Takafumi Kamimura, Shin Iwasaki and Kazuhiko Matsumoto: 49th Electronic Materials Conference, University of Notre Dame, Indiana, USA, June 20 - 22, 2007.

Room Temperature CNT Single Electron Transistor Formed by Plasma Induced Defect Process, \*Shin Iwasaki, Takafumi Kamimura, Masatoshi Maeda, Kazuhiko Matsumoto and Noboru Miura: 49th Electronic Materials Conference, University of Notre Dame, Indiana, USA, June 20 - 22, 2007.

High-sensitive Label-free Biosensors Based on Carbon Nanotube Field-effect Transistors Modified with Aptamers, \*K. Maehashi, T. Katsura, K. Matsumoto, K.

Kerman, Y. Takamura and E. Tamiya: 2007 NSTI Nanotechnology Conference and Trade Show, Santa Clara, California, USA, May 20-24, 2007.

Coulomb Oscillations at Room-Temperature of Single-Walled Carbon Nanotube Field-Effect Transistors (poster), \*Y. Ohno, Y. Asai, K. Maehashi, K. Inoue and K. Matsumoto: 2007 NSTI Nanotechnology Conference and Trade Show, Santa Clara, California, USA, May 20-24, 2007.

Quantum Nano Devices using Carbon Nanotube, \*K. Matsumoto and T. Kamimura: 31th Workshop on Compound Semiconductor Devices and Integrated Circuits, Venice, Italy, May 20-23, 2007.

Effects by Low-Energy Ion Irradiation in Transport Characteristics of n-type Carbon Nanotube Field-Effect Transistors with Passivation Films (poster), \*Kohei Nishiguchi, Yasuhide Ohno, Kenzo Maehashi, Koichi Inoue, Kazuhiro Yamamoto, Kazuhiko Matsumoto: 2008 International Conference On Nanoscience and Nanotechnology, Melbourne, Australia, February 25 - 29, 2008.

Coulomb Oscillation of Single-Walled Carbon Nanotube Field-Effect Transistors with Insulator (poster), \*Yoshihiro Asai, Yasuhide Ohno, Kenzo Maehashi, Koichi Inoue, Kazuhiko Matsumoto: 2008 International Conference On Nanoscience and Nanotechnology, Melbourne, Australia, February 25 - 29, 2008.

High-Performance Local-Electrolyte-Gated Carbon Nanotube Field-Effect Transistors (poster), \*Taiji Katsura, Yasuki Yamamoto, Kenzo Maehashi, Kazuhiko Matsumoto: 2008 International Conference On Nanoscience and Nanotechnology, Melbourne, Australia, February 25 - 29, 2008.

High-Sensitive Label-Free Prostate Specific Antigen Sensors Based on Carbon Nanotube Electrodes, \*Kenzo Maehashi, Kazuhiko Matsumoto, yuzuru Takamura, Eiichi Tamiya: 2008 International Conference On Nanoscience and Nanotechnology, Melbourne, Australia, February 25 - 29, 2008.

Carbon Nanotube Amperometric Biochips With Micro Multi-Pumps, \*Yuichi Tsujita, Kenzo Maehashi, Kazuhiko Matsumoto, Miyuki Chikae, Soichiro Torai, Yuzuru Takamura, Eiichi Tamiya: 2008 International Conference On Nanoscience and Nanotechnology, Melbourne, Australia, February 25 - 29, 2008.

Suppression of Current Fluctuations in Carbon Nanotube Field-Effect Transistors, \*Yasuhide Ohno, Kenzo Maehashi, Koichi Inoue, Kazuhiko Matsumoto: 2008 International Conference On Nanoscience and Nanotechnology, Melbourne, Australia, February 25 - 29, 2008.

The Effect of Charged Ions for Bio-molecule Sensing Using Carbon Nanotube Field-Effect Transistors (poster), \*Y. Yamamoto, T. Katsura, K. Maehashi, Y. Ohno, K. Inoue and K. Matsumoto: 11th SANKEN, 6th Nanotechnology Center and 1st MSTEC International Symposium, Awaji, Japan, February 4 - 5, 2008.



Defect-Induced Plasma Process for Room-Temperature Carbon Nanotube Single-Electron Transistors (poster), \*S. Iwasaki, M. Maeda, T. Kamimura, Y. Ohno, K. Maehashi and K. Matsumoto: 11th SANKEN, 6th Nanotechnology Center and 1st MSTEC International Symposium, Awaji, Japan, February 4 - 5, 2008.

Low-Energy Ion Implantation Effects on n-type Carbon Nanotube Field-Effect Transistors with Passivation Films (poster), \*S. Nagaso, K. Nishiguchi, Y. Ohno, K. Maehashi, K. Inoue, K. Yamamoto and K. Matsumoto: 11th SANKEN, 6th Nanotechnology Center and 1st MSTEC International Symposium, Awaji, Japan, February 4 - 5, 2008.

Microfluidic Carbon Nanotube Biochips with Pneumatic Micro Pumps (poster), \*Y. Tsujita, K. Maehashi, K. Matsumoto, M. Chikae, S. Torai, Y. Takamura and E. Tamiya: 11th SANKEN, 6th Nanotechnology Center and 1st MSTEC International Symposium, Awaji, Japan, February 4 - 5, 2008.

Carbon Nanotube Devices and Applications (invited), \*K. Matsumoto: Nano and Giga Challenges in Electronics and Photonics From Atoms to Materials to Devices to System Architecture.

Single-walled carbon nanotube-based biosensors for label-free detection of protein (poster), \*K. Maehashi, K. Matsumoto: Second SANKEN- CNU Joint Symposium on Nanoscience and Nanotechnology.

Aptamer-based Biosensing Using Optical and Electrical Properties of Nanomaterials, \*Kagan Kerman, Do-Kyun Kim, Kenzo Maehashi, Taiji Katsura, Miyuki Chikae, Shohei Yamamura, Yuzuru Takamura, Kazuhiko Matsumoto and Eiichi Tamiya: 2007 Material Research Society Spring Meeting.

Label-free biosensing based on carbon nanotube devices (invited), \*K. Maehashi, K. Matsumoto: Int. Carbon Nanotube Conference in NU.

### **Publications in Domestic Meetings**

The Japan Society of Applied Physics

15 papers

### **Academic Degrees**

#### **Master Degree of Engineering**

Y. Asai      Carbon Nanotube Single-Electron-Transistors with Al Tunneling Junctions operated at Room Temperatures.

T. Katsura      Protein Sensing by use of Carbon Nanotube Field-Effect-Transistors

K. Nishiguchi      Effects of Ion Irradiation on Carbon Nanotube Field-Effect-Transistors

### **Sponsorships**

#### **Grant-in -Aid for Basic Research (C)**

|            |                                                                                                 |            |
|------------|-------------------------------------------------------------------------------------------------|------------|
| K.Inoue    | Study on the Carbon Nanotubes by Double-Excitation Method                                       | ¥1,820,000 |
| K.Maehashi | Fabrication of High-Sensitive Multi-Biosensors based on Carbon Nanotube-Arrayed Microelectrodes | ¥2,860,000 |

**Other Research Fund**

|             |                                                             |                                                                          |             |
|-------------|-------------------------------------------------------------|--------------------------------------------------------------------------|-------------|
| K.Matsumoto | Japan Science and Technology Agency                         | Carbon nanotube single electron electron single spin measurement systems | ¥65,000,000 |
| K.Matsumoto | New Energy & Industrial Technology Development Organization | Development of CNT High Sensitive Biosensor for Personal QOL System      | ¥18,000,000 |

## Department of Condensed Matter Physics

Professor: Hiroshi KATAYAMA-YOSHIDA  
Associate Professor: Yoshitada MORIKAWA  
Research Technical Expert: Akira YANASE  
Guest Professor: Mitsuhiro MOTOKAWA  
Post Doctoral Fellows: Van An DINH, Ikutaro HAMADA, Susumu YANAGISAWA  
Graduate Students: Hidetoshi KIZAKI, Masayuki TOYODA,  
Tetsuya FUKUSHIMA, Hideki HAYASHIDA,  
Kenji TOYODA, Haruhiko DEKURA, Kunihiro HARADA,  
Motohiko ETO, Yousuke NAKANO,  
Hironobu YAMAGUCHI, Akihumi UOZUMI,  
Hideyuki JIPPOU, Jun ISHISADA, Hitoshi FUJII  
Under Graduate Students: Yuki TERATANI, Ryusuke TOMINAGA  
Supporting Staff: Mika ASADA, Ryoko ITO

### Outlines

The primary activities of this department are theoretical study of electronic properties of condensed matters, and materials design, which predicts novel materials possessing desired properties for applications. In addition to model analyses which extract the essence of materials properties, quantum simulations are used for the study, with the methods of computational physics reflecting a recent remarkable progress of computing ability. Theoretical approaches are tried to predict materials which meet requirements from application areas by first-principles calculations using atomic numbers only as parameters.

### Current Research Project

#### ***Ab initio* Molecular Dynamic Simulation under the Electronic Excitation and Materials Design by Electronic Excitation**

We have developed new simulation method for the application of the electronic excitation-induced atomic migration, and applied for the materials design to use the atomic migration through the meta-stable atomic position. We have designed new fabrication process from graphite to diamond at the normal condition by using the core electron excitations, laser excitation and electron beam excitation. We have simulated the enhancement of the atomic diffusion of boron (B), hydrogen (H), and oxygen (O) in silicon under the electronic excitation in order to fabricate the future nano-electronics materials.

#### **Materials Design for Semiconductor Spintronics.**

Based upon *ab initio* electronic structure calculation, we have proposed the materials design to control the spin interaction for II-VI and III-V compound semiconductors. We have designed the transparent half-metallic ferromagnets for GaN-, AlN-, ZnO-, ZnS-based diluted magnetic semiconductors. We also design the p-type and n-type carrier-concentration dependence of Curie temperature ( $T_C$ ) and 3d transition atom

dependence of  $T_C$  in above diluted ferromagnetic semiconductors. We propose materials design of ferromagnetic diamond without any transition metal elements based on first principles calculations. The electronic structure and the magnetic properties of impurities-doped diamond are calculated by using the Korringa-Kohn-Rostoker method within the local spin density approximation with taking into account disorder using coherent potential approximation. It is found that H atoms which are doped into tetrahedral interstitial sites show finite local magnetic moments. Moreover, the impurities-doped diamond show ferromagnetism with half-metallic density of states. We have determined the magnetic ground states of non-3d transition metal impurity doped CaO, BaO and SrO. We have proposed a new class of high- $T_C$  diluted magnetic semiconductors, which is transparent for our visible light. Based upon the deep impurity band engineering by controlling the correlation energy and impurity band width, we can stabilize the half-metallic ferromagnetism without magnetic impurities such as 3d-transition metal or rare-earth metal impurities.

We show that spinodal decomposition phase in dilute magnetic semiconductors (DMS) offers the possibility to have high Curie temperatures ( $T_C$ ) even if the magnetic exchange interaction is short ranged. The spinodal decomposition is simulated by applying the Monte Carlo method to the Ising model with realistic (*ab initio*) chemical pair interactions between magnetic impurities in DMS. Curie temperatures are estimated by the random phase approximation with taking disorder into account. It is found that the spinodal decomposition phase inherently occurs in DMS due to strong attractive interactions between impurities. This phase decomposition supports magnetic network over the dimension of the crystal resulting in a high- $T_C$  phase.

The electronic structures and the magnetic properties of dilute magnetic semiconductors (DMSs) based on transparent semiconducting oxide  $\text{CuAlO}_2$  are calculated by using the Korringa-Kohn-Rostoker method combined with the coherent potential approximation (KKR-CPA) within the local density approximation. We see from the results that we can expect to obtain the half-metallic and high-spin ferromagnetic state is expected to be stable in Mn-, Fe-, Co- and Ni-doped  $\text{CuAlO}_2$ .

#### **Materials Design and Valence Control of Wide Band-gap Semiconductors.**

Based upon *ab initio* electronic structure calculation, we have proposed codoping method for the fabrication of the low-resistive p-type  $\text{CuAlO}_2$ , and n-type diamond. Our predictions of co-doping for the valence control are confirmed by the experiment. We have calculated the formation energy of P, N, and B in diamond, and oxygen-interstitial, Cu-vacancy, Al-vacancy, Be-acceptor, Mg-acceptor in  $\text{CuAlO}_2$ . We also proposed the possibility of high efficient thermoelectric material ( $ZT > 3$ ) and transparent superconductivity upon slightly p-type or heavily p-type doped  $\text{CuAlO}_2$ .

#### **Design of High- $T_C$ Nano-superstructure for Spintronics by Spinodal Decomposition**

We show that spinodal decomposition phase in dilute magnetic semiconductors (DMS) offers the possibility to have high Curie temperatures ( $T_C$ ) even if the magnetic exchange interaction is short ranged. The spinodal decomposition is simulated by applying the Monte Carlo method to the Ising model with realistic (*ab initio*) chemical pair interactions between magnetic impurities in DMS. Curie temperatures are estimated by the random phase approximation with taking disorder into account. It is found that the spinodal decomposition phase inherently occurs in DMS due to strong attractive

interactions between impurities. This phase decomposition supports magnetic network over the dimension of the crystal resulting in a high- $T_C$  phase.

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### **Design of High-efficient Thermoelectric Materials**

Based upon *ab initio* electronic structure calculation, we have developed the design method for high-efficient thermoelectric materials and applied to explain the existing and available experimental data for PbTe and Bi<sub>2</sub>Te<sub>3</sub> compounds. We obtained good agreement between the calculation and experiment. We have design high-efficient thermoelectric power for p-type CuAlO<sub>2</sub>.

### **Materials Design for the High-efficient Silicon Solar Cells.**

We have proposed a mechanism of CN diffusion and termination of defect states in Si by using *ab initio* molecular dynamics simulations. In this mechanism, CN diffuses in the Si network by changing the bond orders of CN bond between single and double bonds giving rather small diffusion barriers. This makes CN diffusion to defect sites very efficient and is important for defect states termination by CN treatment.

### **Hydrogen at Water/Metal Interfaces.**

Density functional theory calculations were carried out on hydrogen adsorbed on the Pt(111) electrode in an electrochemical environment, by taking into account electric field, solvent, and hydrogen coverage effects. We find that the field effect on the adsorption energies and vibrational frequencies of hydrogen on Pt is negligibly small and vibrational Stark tuning rate is about 10 cm<sup>-1</sup>V<sup>-1</sup> at low coverages and becomes slightly larger ( $\approx 20$  cm<sup>-1</sup>V<sup>-1</sup>) at high coverages in the ultra high vacuum. By explicitly including water molecules, the potential energy surface of hydrogen on Pt surface is significantly modified, and it is strongly depends on the orientation of water molecules. By including the solvent effect on the Pt-H stretching frequency, the Stark tuning rate is increased further to  $\approx 50$  cm<sup>-1</sup>V<sup>-1</sup>. But it is still smaller than the experimentally observed value of 130 cm<sup>-1</sup>V<sup>-1</sup>. On the other hand, Pt-H stretching frequency rapidly decreases by increasing the hydrogen coverage. The results presented in this work clearly show that it is necessary to take into account electric field, water solvent and hydrogen coverage effects to fully account for the experimentally observed large potential dependence of the Pt-H stretching frequency.

### **Organic/Metal Interfaces**

In the present study, we have examined the IDIS model for a simple C<sub>6</sub>H<sub>6</sub>/Al(111) interface and compared it with self-consistent density functional theory (DFT) calculations. The vacuum level shift from a simple induced density of interface state

(IDIS) model ( $\Delta_{\text{IDIS}}$ ) agrees rather well with that calculated by self-consistent DFT-GGA calculations ( $\Delta_{\text{GGA}}$ ) in weakly interacting cases, where the distance between the molecule and the substrate ( $Z_{\text{C}}$ ) is larger than about 0.3 nm. But the  $\Delta_{\text{IDIS}}$  deviates from the  $\Delta_{\text{GGA}}$  for  $Z_{\text{C}}$  smaller than 0.3 nm. The real space distribution of the induced charge density due to the interaction between  $\text{C}_6\text{H}_6$  and Al substrate is much more complicated than that assumed in the simple IDIS model even in weakly interacting cases. At present, it is not clear why such a simple model works reasonably well to describe the vacuum level shift for weakly interacting organic/metal interfaces and further investigations are necessary to constitute a more robust interface model.

### **Investigation of switching behavior of molecules on metal electrodes for molecular-scale electronics.**

In order to investigate the effect of electric field on the adsorption state and electronic properties of organic molecules adsorbed on metal surfaces, we have carried out density functional calculations for thiolate molecules adsorbed on Au(111) surfaces. We also investigated benzene thiolate and benzene selenolate on Pt(111) surfaces to compare electronic structures of those molecules on metals. Furthermore, we investigated adsorption state of DBP-S molecule which is promising properties of organic molecules connecting metal electrodes and organic functional groups.

### **Elucidation of mechanism of intelligent catalyst for three-way catalysts.**

We have investigated the stability of dissolution of Pd, Rh, and Pt precious metals into perovskite oxides such as  $\text{LaFeO}_3$  and  $\text{CaTiO}_3$  to investigate the mechanism of prevention of sintering effect in intelligent catalysts. By combining thermodynamics/statistical mechanics with quantum simulations, we successfully reproduced trends of stability of solid-solution of precious metals into perovskite oxides. We are now further investigating those materials to investigate the metal-oxide/metal interface to further investigate the reaction mechanism.

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Design of colossal solubility of magnetic impurities for semiconductor spintronics by using the co-doping method (poster), K. Sato and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Spinodal decomposition in (In, Ga)N (poster), M. Eto, M. Toyoda, K. Sato and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Ab-initio Materials Design of CuAlO<sub>2</sub>-based Diluted magnetic Semiconductors (poster), H. Kizaki, K. Sato and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

First Principle Material Design of High- $T_c$  Half-Metallic Half-Heusler Alloys (poster), V. A. Dinh, K. Sato and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Electric Field Effect on the Atomic Geometries and Electronic Structures of Adsorbed Molecules on Metal Surfaces (poster), Y. Morikawa, A. Nagoya, H. Jippou and I. Hamada: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Improvement of the gettering efficiency of Cu by BO complexes (poster), K. Shirai, K. Matsukawa, H. Yamaguchi, H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

The effects of monovacancy on the elastic properties of Si (poster), J. Ishisada, K. Shirai and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

The stable site and electronic states of Copper in Silicon (poster), H. Yamaguchi, K. Shirai, H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

The theoretical study of elemental solid Boron under high pressure (poster), H. Dekura, K. Shirai and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

First-principles Study of Hydrogen on Pt(111) in an Electrochemical Condition (poster), I. Hamada, Y. Morikawa: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

First-principles theoretical study of  $\text{Alq}_3$  on Al and Mg surfaces (poster), S. Yanagisawa, K. Lee and Y. Morikawa: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Computational Nano-materials Design for Spin-Currents Control in Semiconductor Nano-spintronics (invited), H. Katayama-Yoshida, T. Fukushima, M. Toyoda, H. Kizaki, V. A. Dinh and K. Sato: 3rd Indo-Japan Conference on Ferroics and Multiferroics (under the aegis of DST-JSPS Program), Kolkata, Indo, February 4-6, 2008.

Computational nano-materials design for spin-currents control in semiconductor nano-spintronics (invited), H. Katayama-Yoshida: SPIN CURRENTS 2008, Sendai, Japan, February 18-19, 2008.

First-principles Study on the Magnetic Interactions in ZnO-based Dilute Magnetic Semiconductors (poster), M. Toyoda, H. Akai, K. Sato and H. Katayama-Yoshida: APS, AmericanPhysical Society March Meeting, New Orleans, USA, March 10-14, 2008.

Design of Colossal Solubility of Magnetic Impurities for Semiconductor Spintronics by the co-doping Method, T. Fukushima, K. Sato and H. Katayama-Yoshida: APS, AmericanPhysical Society March Meeting, New Orleans, USA, March 10-14, 2008.

Computational Nano-materials Design for Spin-Currents Control in Semiconductor Nano-Spintronics, H. Katayama-Yoshida, T. Fukushima, V. A. Dinh and K. Sato: APS, AmericanPhysical Society March Meeting, New Orleans, USA, March 10-14, 2008.

First-Principles Study on Electronic Structure of  $\text{TiO}_2$  based Dilute Magnetic Semiconductors, H. Kizaki, M. Toyoda, K. Sato and H. Katayama-Yoshida: APS, AmericanPhysical Society March Meeting, New Orleans, USA, March 10-14, 2008.

First-principles Simulations of Metal/Organic Interfaces: Importance of Weak Interaction (invited), Y. Morikawa: 2008 Materials Research Society (MRS) Spring Meeting, San Francisco, USA, March 24-28, 2008.

Improvement of the gettering efficiency of Cu by BO complexes (poster), K. Shirai, K. Matsukawa, N. Yamaguchi, H. Katayama-Yoshida: The Forum on the Science and Technology of Silicon Materials 2007, Niigata, JAPAN, Nov.12-14, 2007.

Effect of monovacancy on the elastic constant of crystalline silicon (poster), J. Ishisada, K. Shirai, H. Dekura and H. Katayama-Yoshida: The Forum on the Science and



Technology of Silicon Materials 2007, Niigata, JAPAN, Nov.12-14, 2007.

The stable site and electronic states of Cu in Si (poster), H. Yamaguchi, K. Shirai and H. Katayama-Yoshida: The Forum on the Science and Technology of Silicon Materials 2007, Niigata, JAPAN, Nov.12-14, 2007.

### **Contributions to International Conferences and Journals**

|                     |                                                                                                                                                                                    |
|---------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| H. Katayama-Yoshida | 24 <sup>rd</sup> International Conference on Defects in Semiconductors : ICDS24 (Advisory committee members)                                                                       |
| H. Katayama-Yoshida | The First international conference on Quantum Design and simulation (Organizing Committee)                                                                                         |
| H. Katayama-Yoshida | 4 <sup>th</sup> International Conference on Physics and Application of Spin-related Phenomena in Semiconductors: PASPS-VI (International Advisory Committee and Program Committee) |
| Y. Morikawa         | International Symposium on Theories of Organic/Metal Interfaces 2007 (ISTOMI07), (Conference Chair)                                                                                |

### **Publications in Domestic Meetings**

|                                                                                                                      |          |
|----------------------------------------------------------------------------------------------------------------------|----------|
| The Physical Society of Japan                                                                                        | 16paper  |
| The Japan Society of Applied Physics                                                                                 | 9papers  |
| The 12 <sup>th</sup> symposium on the Physics and Application of Spin-Related Phenomena in Semiconductors (PASPS-12) | 7 papers |
| Others                                                                                                               | 4papers  |

### **Academic Degrees**

#### **Doctor Degree for Science**

|              |                                                                                                                                                                 |
|--------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| H. Kizaki    | First-Principles Materials Design for Oxide Based Semiconductor Spintronics                                                                                     |
| M. Toyoda    | Development and Application of Self-interaction Correction in First-principles Electronic Structure Calculations to Design New Materials for Spintronic Devices |
| T. Fukushima | <i>Ab initio</i> and Statistical Investigations of Electronic Structure and Finite Temperature Magnetism in Dilute Magnetic Semiconductors                      |

#### **Master Degree for Engineering**

|           |                                                                                         |
|-----------|-----------------------------------------------------------------------------------------|
| Y. Nakano | Theoretical research of interfacial dipole at benzene/metal, pentacene/metal interfaces |
|-----------|-----------------------------------------------------------------------------------------|

#### **Master Degree for Science**

|              |                                                                                                             |
|--------------|-------------------------------------------------------------------------------------------------------------|
| M. Eto       | <i>Ab initio</i> Design of Nano-structure in $\text{In}_x\text{Ga}_{1-x}\text{N}$ by Spinodal Decomposition |
| H. Yamaguchi | The stable site and electronic states of Cu in Si                                                           |

### **Sponsorship**

**Grant-in-Aid for Scientific Research on Priority Areas**

|             |                                                                            |             |
|-------------|----------------------------------------------------------------------------|-------------|
| Y. Morikawa | Development and releasing of quantum simulator for submicron scale systems | ¥2,300,000  |
| Y. Morikawa | Development of efficient parallel quantum dynamics simulator               | ¥12,700,000 |
| Y. Morikawa | Theory of nano-scale linked molecules                                      | ¥2,900,000  |
| Y. Morikawa | Design of new multi-functional nanotube device                             |             |

**Entrusted Research**

|             |                                                                                                  |                                                                                            |             |
|-------------|--------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|-------------|
| Y. Morikawa | Japan Science and Technology Corporation<br>Core Research for Evolutional Science and Technology | Contact effects and transport properties of single molecules                               | ¥10,110,100 |
| Y. Morikawa | Japan Science and Technology Corporation<br>Core Research for Evolutional Science and Technology | Electrode Chemistry at Interfaces Between Two Phases                                       | ¥12,010,000 |
| Y. Morikawa | Japan Science and Technology Corporation.<br>Elements Science and Technology Project             | Elucidation and design of self-organization for nano-scale catalysts from first-principles |             |

**Other Research Fund**

|                     |                                          |                                                                 |            |
|---------------------|------------------------------------------|-----------------------------------------------------------------|------------|
| H. Katayama-Yoshida | Japan Science and Technology Corporation | Case study on advanced measurements and analysis                | ¥1,960,000 |
| H. Katayama-Yoshida | Japan Atomic Energy Agency               | Analysis and Materials design simulation in Grid computing      |            |
| Y. Morikawa         | Toyota Central R&D Labs., INC.           | Development of LDA+U method for calculation of oxide catalysts. | ¥1,800,000 |
| Y. Morikawa         | Matsushita Electric Industrial Co., Ltd. | First-principles investigation of metal/organic interfaces      | ¥1,500,000 |
| Y. Morikawa         | Kobe Steel Ltd.                          | First-principles investigation of atomic structures and         | ¥1,045,000 |

electronic properties of  
interfaces.

# Division of Advanced Materials Science and Technology

## Outline

The Division of Advanced Materials Science and Technology is composed of six departments with research fields: Structural Characterization and Design, Metallic Materials Process, Atomic Scale Science, Functional Ceramic Materials, Frontier Materials Creation, and Advanced-Energy Materials. This division has a close relationship with Nanoscience and Nanotechnology Center of this Institute founded in 2002. The future highly functionalized materials can be obtained by hybridizing different kinds of materials which are well designed and controlled with respect to their structures, dimensions and physical and chemical properties. We are aiming at design, development and characterization of new functional or high strength and high performance materials by means of highly advanced processes with micro, nano and atomic scale controlled techniques we developed.

## Achievements

- Local structural changes on annealing in Fe-based metallic glasses
- Low Temperature Synthesis of  $L1_0$ -FePd Nanocrystals by Co Addition
- Radiation Tolerance in Structurally-Related Oxides
- Development of mass production method of lotus-type porous carbon steel by means of continuous casting technique and application to light-weight and vibration damping parts of machinery tools
- Invention of lotus-type porous metals through thermal decomposition method of compounds containing gas elements
- Fabrication of nano-sized hollow sphere metals through Kirkendall effect in atomic diffusion
- Construction of function harmonized superlattices, ferromagnetic oxide heterostructures with for highly sensitive spin devices for external fields
- Nano-science by using of scanning probe microscopes towards high resolution imaging of a single molecule of DNA and a protein.
- Development of bio-molecular device constructed from DNA.
- Development of low temperature fabrication method of  $\text{SiO}_2/\text{Si}$  structure by use of nitric acid oxidation and its application to TFT
- Development of defect passivation semiconductor cleaning method and improvement of device characteristics
- Development of low temperature oxidation method of SiC and improvement of characteristics of SiC-based MOS devices
- Development of multi-functional ceramic and polymer nanocomposites by low-dimensional nano-structural control and their application
- Multi-functionalization of oxide nanotubes and their application for energy/environmental systems
- Creation of novel phases of solids via photoinduced phase transitions
- Photoinduced structural instability on semiconductor surfaces
- Ultra fast carrier dynamics on semiconductor surfaces

## Department of Structural Characterization and Design

|                        |                                                                                 |
|------------------------|---------------------------------------------------------------------------------|
| Professor:             | Yoshihiko HIROTSU                                                               |
| Associate Professor:   | Manabu ISHIMARU                                                                 |
| Research Associate:    | Akihiko HIRATA, Kazuhisa SATO (-2007.10.31)                                     |
| Post Doctoral Fellows: | Andras KOVACS, Jonghan WON                                                      |
| Graduate Students:     | Han Wool RYU, Naoto KAWAHARA, Yousuke KIMURA<br>Fumihiko NAKAMURA, Dai YAMAMOTO |
| Supporting Staff:      | Shigeko TOMII                                                                   |

### Outlines

In controlling structures of new functional materials, introduction of new local structure analysis techniques to the materials becomes necessary. Using high-resolution electron microscopy (HREM), electron diffraction and electron energy-loss spectroscopy, we are mainly analysing local atomic structures and electronic states of functional alloy nano-particles, amorphous alloys, ion-irradiated ceramics and multi-layered materials. We are also developing new local structure analysis techniques using nano-sized electron probe, energy-filter and imaging-plate. Molecular dynamics and Monte-Carlo calculations and electronic band structure calculations of new materials are carried out for predicting their structures and physical properties.

### Current Research Project

#### Local structural changes on annealing in Fe-based metallic glasses

We have examined local structural changes on annealing including crystallization behavior especially in Fe-based metallic glasses by means of transmission electron microscopy. The following results were obtained this year. (1) In an FeCoSiBNb bulk metallic glass, a nanocrystalline microstructure with complex  $\text{Fe}_{23}\text{B}_6$ -type crystals was obtained by annealing around the crystallization temperature. Structural features of medium range order (MRO) found in as-quenched and annealed (at lower than the glass transition temperature ( $T_g$ )) glass states are different from those of the primary crystalline phase. During the annealing around  $T_g$ , the crystalline order begins to appear when the grain size reaches around 5 nm. (2) In an FeSiBP bulk metallic glass, precipitates with an one-dimensional long period structure were found to appear from the glass state at the crystallization temperature. The annealing at lower than  $T_g$  induced a development of the MRO regions which have no structural similarity with the crystalline phase. From above results, we concluded that existence of the characteristic MRO structures as well as the complex primary phases contributes to difficulty in making the crystalline nuclei in the bulk metallic glasses.

#### Low Temperature Synthesis of $\text{L1}_0$ -FePd Nanocrystals by Co Addition

$\text{L1}_0$ -PdCoFe nanoparticles were prepared by vapor deposition of the components and characterized by transmission electron microscopy and by superconducting quantum interference device magnetometry. Co addition to the Fe-Pd nanocrystals resulted in a strong perpendicular magnetic anisotropy and a reduction in the formation temperature

of the ordered  $L1_0$  phase. Formation of the ordered phase was studied by *in situ* annealing of specimens inside the transmission electron microscope.  $L1_0$  phase formation started at 698 K, as evidenced by the appearance of 110 superlattice reflections in electron diffraction patterns. Co additions enhanced the magnetic easy axis alignment perpendicular to the film plane. The perpendicular maximum coercivity at room temperature was 1.75 kOe for  $L1_0$ -PdCoFe nanoparticles with an average size of 8 nm, and the magnetic coercivity decreased by increasing the Co concentration in the  $L1_0$  nanoparticles.

### **Radiation Tolerance in Structurally-Related Oxides**

The development of radiation tolerant materials is of technological importance for the immobilization and long-term storage of surplus actinides and high-level radioactive wastes such as spent fuel from nuclear reactors. Complex oxide ceramics represent an important class of candidate materials for nuclear-waste hosts, and therefore much effort has been devoted to assess radiation damage behavior in these materials. In this year, we examined the radiation damage behavior of various complex oxides which themselves are related by structure. Two important points are made in this paper: (1) a temperature-composition (T-C) phase diagram is a good indicator for radiation damage tolerance properties (in particular, amorphization resistance); and (2) the O-D fluorite defect reaction pair is a good indicator of T-C phase diagram features (and consequently, of radiation tolerance). The first concept can be used immediately to make radiation damage predictions for systems that contain parent fluorite phases in their T-C phase diagrams (cerates, hafnates, thorates, uranates, plutonates, and higher actinides).

## **Publications**

### **Original Papers**

Direct Imaging of Local Atomic Ordering in a Pd-Ni-P Bulk Metallic Glass using Cs-Corrected Transmission Electron Microscopy, A. Hirata, Y. Hirotsu, T. G. Nieh, T. Ohkubo, N. Tanaka: *Ultramicroscopy*, 107 (2007) 116-123.

Mössbauer Study of Ultrathin Fe/Al Multilayer Films, D. Kaptás, J. Balogh, T. Kemény, L. F. Kiss, L. Bujdosó, A. Kovács, A. Hirata, I. Vincze: *Phys. Rev. B*, 75 (2007) 014417(1)- 014417(9).

Local Atomic Structure Analysis of Zr-Ni and Zr-Cu Metallic Glasses using Electron Diffraction, A. Hirata, T. Morino, Y. Hirotsu, K. Itoh, T. Fukunaga: *Mater. Trans.*, 48 (2007) 1229-1303.

Voronoi Analysis of the Structure of Ni-Zr-Al Ternary Metallic Glass, T. Fukunaga, K. Itoh, T. Otomo, K. Mori, M. Sugiyama, H. Kato, M. Hasegawa, A. Hirata, Y. Hirotsu, A. C. Hannon: *Mater. Trans.*, 48 (2007) 1698-1702.

Structural Analysis of BiFeO<sub>3</sub> Polycrystalline Films by Transmission Electron Microscopy, H. Naganuma, A. Kovács, A. Hirata, Y. Hirotsu, S. Okamura: *Mater. Trans.*, 48 (2007) 2370-2377.

Fabrication of L10-PdCoFe Nanocrystalline Particles with Tilted Magnetic Easy Axis, A. Kovács, Y. Hirotsu: Appl. Phys. Lett., 91 (2007) 193106(1)- 193106(3).

Melt-Spun L10 Fe-Pt-(Zr, Nb and Ti)-B Nanocrystalline Alloys with High Coercivity, A. Makino, T. Bitoh, A. Inoue, Y. Hirotsu: Mater. Sci. Eng. A, 449-451 (2007) 66-70.

Magnetic Properties and Structure of Fe-Pt-M-B (M=Zr, Nb and Ti) Alloys Produced by Quenching Technique, A. Makino, T. Bitoh, A. Inoue, Y. Hirotsu: J. Alloys Comp., 434-435 (2007) 614-617.

Magnetic Properties and Microstructure of FePt-M-B (M=Zr, Nb, La) Films, H. Okumura, S. Nishinakagawa, T. Bitoh, A. Makino, K. Sato, Y. Hirotsu: J. Magn. Magn. Mater., 310 (2007) 2527-2528.

Particle Size Dependence of Atomic Ordering and Magnetic Properties of L10-FePd Nanoparticles, H. Naganuma, K. Sato, Y. Hirotsu: J. Magn. Magn. Mater., 310 (2007) 2356-2358.

Strong Perpendicular Magnetic Anisotropy of Fe-Pd Nanocrystalline Particles Enhanced by Co Addition, A. Kovács, K. Sato, Y. Hirotsu: J. Appl. Phys., 101 (2007) 033910(1)-033910(4).

Low-Temperature Atomic Ordering of Oriented L10-FePtCu Nanoparticles with High Areal-Density Characterized by Transmission Electron Microscopy and Electron Diffraction, H. W. Ryu, K. Sato, Y. Hirotsu: Mater. Trans., 48 (2007) 903-908.

High-Resolution Transmission Electron Microscopy Analysis of L10 Ordering Process in Fe/Pd Thin Layers, A. Kovács, K. Sato, Y. Hirotsu: J. Appl. Phys., 102 (2007) 123512(1)-123512(4).

Improvement of Structural and Magnetic Properties of L10-FePd Nanocrystals by Co Addition, A. Kovács, K. Sato, Y. Hirotsu: IEEE Trans. Mag., 43 (2007) 3097-3099.

Size-Dependent Structural Transition from Multiple-Twinned Particles to Epitaxial fcc Nanocrystals and Nanocrystal Decay, K. Sato, W. J. Huang, F. Bohra, S. Sivaramakrishnan, A. P. Tedjasaputra, J. M. Zuo: Phys. Rev. B, 76 (2007) 144113(1)-144113(8).

Synthesis of Iron Silicides by Electron-Beam Evaporation: Effects of Substrate Pre-Baking Temperature and Fe Deposition Thickness, J. H. Won, K. Sato, M. Ishimaru, Y. Hirotsu: Jpn. J. Appl. Phys., 46 (2007) 732-737.

Radiation-Induced Amorphization Resistance and Radiation Tolerance in Structurally Related Oxides, K. E. Sickafus, R. W. Grimes, J. A. Valdez, A. Cleave, M. Tang, M. Ishimaru, S. M. Corish, C. R. Stanek, B. P. Uberuaga: Nature Mater., 6 (2007) 217-223.

Effect of Ionization Rates on Dynamic Recovery Processes during Electron-Beam

Irradiation of 6H-SiC, I.-T. Bae, W. J. Weber, M. Ishimaru, Y. Hirotsu: Appl. Phys. Lett., 90 (2007) 121910(1)-121910(3).

Exchange Interactions in Hydrogen-Induced Amorphous YFe<sub>2</sub> (invited), K. Suzuki, K. Ishikawa, K. Aoki, J. M. Cadogan, M. Ishimaru, Y. Hirotsu: J. Non-Cryst. Solids, 353 (2007) 748-752.

Post-Annealing Recrystallization and Damage Recovery Process in Fe Ion Implanted Si, M. Naito, A. Hirata, M. Ishimaru, Y. Hirotsu: Nucl. Instrum. Meth. B, 257 (2007) 340-343.

Surface Sputtering in High-Dose Fe Ion Implanted Si, M. Ishimaru: Nucl. Instrum. Meth. B, 258 (2007) 490-492.

Ion-beam-induced phase transformations in delta-Sc<sub>4</sub>Zr<sub>3</sub>O<sub>12</sub>, M. Ishimaru, Y. Hirotsu, M. Tang, J. A. Valdez, K. E. Sickafus: J. Appl. Phys., 102 (2007) 063532(1)-063532(7).

Formation process of sharp-pointed structures on GaN nanorods during RF-MBE growth and their field emission characteristics, M. Terayama, S. Hasegawa, K. Uchida, M. Ishimaru, Y. Hirotsu, H. Asahi: Physica Status Solidi C, 4 (2007) 2371-2374.

Formation processes of iron silicide nanoparticles studied by ex situ and in situ transmission electron microscopy, J. H. Won, A. Kovács, M. Naito, M. Ishimaru, Y. Hirotsu: J. Appl. Phys., 102 (2007) 103512(1)-103512(7).

Change of Nanostructure in (Fe<sub>0.5</sub>Co<sub>0.5</sub>)<sub>72</sub>B<sub>20</sub>Si<sub>4</sub>Nb<sub>4</sub> Metallic Glass on Annealing, A. Hirata, Y. Hirotsu, K. Amiya, N. Nishiyama, A. Inoue: Mater. Sci. Forum, 539-543 (2007) 2077-2081.

Low-Temperature Synthesis of Oriented L10-FePtCu Nanoparticles with High Coercivity, H. W. Ryu, K. Sato, Y. Hirotsu: Solid State Phenom., 124-126 (2007) 855-858.

Structure and Magnetic Properties of Nanocrystalline Pd-Co and Pd-Co-Fe Layers, A. Kovács, K. Sato, Y. Hirotsu: Solid State Phenom., 124-126 (2007) 907-910.

Direct Synthesis of Isolated L10-FePtCu Nanoparticles by RF-Magnetron Sputtering, H. W. Ryu, K. Sato, Y. Hirotsu: Solid State Phenom., 127 (2007) 129-134.

### **Review Papers**

Advanced Electron Beam Techniques, Y. Hirotsu and Y. Yoshida, Hamon 17 (2007) 75-80 (in Japanese).

Local Structure and Crystallization Process of Amorphous Fe-Si Thin Layers, M. Naito, A. Hirata, M. Ishimaru, and Y. Hirotsu, J. Cryst. Soc. Jpn. 49 (2007) 115-121 (in Japanese).



Local Structure Study of Metallic Glasses by Means of Transmission Electron Microscopy, A. Hirata and Y. Hirotsu, J. Cryst. Soc. Jpn. 49 (2007) 122-128 (in Japanese).

Electron Diffraction Structure Analysis of Phase-Change Recording Materials, M. Naito, M. Ishimaru, and Y. Hirotsu, Materia Japan 46 (2007) 652-659 (in Japanese).

Transmission Electron Microscopy Study on Ion-beam-induced Structural Changes in  $\delta$ - $\text{Sc}_4\text{Zr}_3\text{O}_{12}$ , M. Ishimaru, J. Cryst. Soc. Jpn. 49 (2007) 328-334 (in Japanese).

### **International Conferences**

Temperature dependence of electron-beam-induced effects in amorphous apatite (poster), I.-T. Bae, Y. Zhang, W. J. Weber, M. Ishimaru, Y. Hirotsu, M. Higuchi: The 14th International Conference on Radiation Effects in Insulators, Caen-France (August 28-September 1, 2005).

A surprising crystal structure produced by an ion-beam-induced phase transformation in  $\delta$ - $\text{Sc}_4\text{Zr}_3\text{O}_{12}$ , K. E. Sickafus, B. P. Uberuaga, C. R. Stanek, M. Ishimaru, Y. Hirotsu, J. A. Valdez, M. Tang, P. Hosemann, and A. L. Johnson, H. T. Thao: The 14th International Conference on Radiation Effects in Insulators, Caen-France (August 28-September 1, 2005).

Structural characterization of ion-beam-induced amorphous silicon carbide by advanced electron microscopy (invited), M. Ishimaru: 15th International Conference on Surface Modification of Materials by Ion Beams, Mumbai, India (September 30 - October 5, 2007).

In situ TEM study on the formation process of iron silicide nanoparticles on Si substrate (poster), J. H. Won, A. Kovacs, M. Ishimaru, Y. Hirotsu: Materials Research Society 1998 Fall Meeting, Boston, USA (November 26-30, 2007).

Observation of Local Structural Change in the Course of Primary Crystallization of Metallic Glasses (invited), Y. Hirotsu, A. Hirata: 14th International Symposium on Metastable and Nano Materials, Corfu, Greece (August 26-30, 2007).

Medium Range Order Structures and their Changes in the Course of Primary Crystallization in some Metallic Glasses (invited), Y. Hirotsu: WPI & IFCAM Joint Workshop, Sendai (February 18-19, 2008).

Fabrication of Oriented Hard-Magnetic Alloy Nanoparticles and Their Characterization (invited), Y. Hirotsu, K. Sato, A. Kovacs, H. Naganuma, H.W. Ryu: 1st International Symposium on Advanced Magnetic Materials, Jeju, Korea (May 28 - June 1, 2007).

Local Structure Studies of Metallic Glasses using HREM and Electron Diffraction (invited), Y. Hirotsu, A. Hirata, T. Ohkubo: International Workshop on Bulk Metallic Glasses: Science & Technology, Bangalore, India (January 12-17, 2007).

### **Contributions to International Conferences and Journals**

|             |                                                                                                  |
|-------------|--------------------------------------------------------------------------------------------------|
| Y. Hirotsu  | 7 <sup>th</sup> Polish-Japanese Joint Seminar on Micro and Nano Analysis<br>(Advisory Committee) |
| M. Ishimaru | Japanese Journal of Applied Physics (Associate Editor)                                           |

### **Publications in Domestic Meetings**

|                                      |          |
|--------------------------------------|----------|
| The Japan Institute of Metals        | 7 papers |
| The Japan Society of Applied Physics | 3 papers |
| The Japanese Society of Microscopy   | 4 papers |

### **Academic Degrees**

#### **Doctor Degree for Engineering**

|           |                                                                                                                   |
|-----------|-------------------------------------------------------------------------------------------------------------------|
| H. W. Ryu | Low Temperature Synthesis and Characterization of Oriented<br>Hard Magnetic L1 <sub>0</sub> -FePtCu Nanoparticles |
|-----------|-------------------------------------------------------------------------------------------------------------------|

#### **Master Degree for Engineering**

|             |                                                                                   |
|-------------|-----------------------------------------------------------------------------------|
| N. Kawahara | Local Structure and Crystallization Process of Fe-Si-B-P Bulk<br>Metallic Glasses |
| Y. Kimura   | Structural and Magnetic Properties of Hard-Magnetic FePt<br>Nanoparticles         |

### **Sponsorship**

#### **Grant-in-Aid for Scientific Research on Priority Areas (2)**

|            |                                                                                      |            |
|------------|--------------------------------------------------------------------------------------|------------|
| Y. Hirotsu | In situ observation of atomistic structures in<br>metallic liquid and metallic glass | ¥9,800,000 |
|------------|--------------------------------------------------------------------------------------|------------|

#### **Grant-in-Aid for Scientific Research (S)(2)**

|            |                                                                                                         |             |
|------------|---------------------------------------------------------------------------------------------------------|-------------|
| Y. Hirotsu | Fabrication and characterization of hard<br>magnetic alloy nanoparticles produced by vapor<br>quenching | ¥14,430,000 |
|------------|---------------------------------------------------------------------------------------------------------|-------------|

#### **Grant-in-Aid for Scientific Research (C)**

|             |                                                                                     |            |
|-------------|-------------------------------------------------------------------------------------|------------|
| M. Ishimaru | Amorphization and chemical short-range order<br>in SiC under radiation environments | ¥2,730,000 |
|-------------|-------------------------------------------------------------------------------------|------------|

#### **Grant-in-Aid for Encouragement of Young Scientists (B)**

|         |                                                                                                                                                             |            |
|---------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| K. Sato | Quantitative Analyses of Nanostructure and<br>Magnetic Properties of L1 <sub>0</sub> -FePt and FePd<br>Nanoparticles by Transmission Electron<br>Microscopy | ¥2,500,000 |
|---------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|

#### **Entrusted Research**

|            |      |                             |            |
|------------|------|-----------------------------|------------|
| Y. Hirotsu | NEDO | Nano-structure Analysis for | ¥3,150,000 |
|------------|------|-----------------------------|------------|

|            |                                                                             |                                                                                    |          |
|------------|-----------------------------------------------------------------------------|------------------------------------------------------------------------------------|----------|
|            | (Advanced Materials Technology Utilizing Glassy Metals for Commercial Uses) | the Evaluation of Mechanical Properties in Glassy Metals                           |          |
| Y. Hirotsu | Matsushita Electric Works, Ltd.                                             | Structure Characterizatiuon of Inorganic and Organic Materials on Glass Substrates | ¥400,000 |

## Department of Metallic Materials Process

|                            |                                                                                                                                                                                                                                                     |
|----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Professor:                 | Hideo NAKAJIMA                                                                                                                                                                                                                                      |
| Associate Professor:       | Shinsuke SUZUKI                                                                                                                                                                                                                                     |
| Assistant Professor:       | Masakazu TANE, Ryusuke NAKAMURA                                                                                                                                                                                                                     |
| Post Doctoral Fellows:     | Sang-Youl KIM                                                                                                                                                                                                                                       |
| Research Technical Expert: | Yoshitada NAKAI                                                                                                                                                                                                                                     |
| Graduate Students:         | Toshihiko KUJIME, Je-Sung PARK, Takuya IDE<br>Hirofumi OHNISHI, Kelly ALVAREZ, Hironori SEKI<br>Hiroshi CHIBA, Tae-Bum KIM, Shingo AKITA,<br>Kazuyoshi WATANABE, Takehiro WADA,<br>Tae KAWASHIMA, Yuki KAWAMURA<br>Kohta TANIGUCHI, Jong-Seuk JEONG |
| Research Student:          | Juan LOBOS(2007.10.24-2008.11.1)                                                                                                                                                                                                                    |
| Supporting Staff:          | Satoko MATSUMOTO                                                                                                                                                                                                                                    |

### Outlines

Metals are fundamental materials indispensable to various structural and functional materials. The main purpose of this department is to investigate physics of metallic materials and develop novel processing of the metallic materials. The department has undertaken the following several topics of the metallic materials science and engineering.

Lotus-type porous metals (lotus metals) developed by this department are unique materials which exhibit extraordinary superior mechanical strength. The materials have been fabricated by unidirectional solidification of the melts under pressurized gases. In this year, we developed a novel safe and low-cost method for fabricating lotus metals without pressurized gas. And the mechanical properties of lotus-type porous metals were investigated to develop lotus metals with improved strength. Then light-weight structural materials of lotus aluminum alloys and lotus carbon steel, and biomedical materials of lotus Ni-free stainless steel were developed for practical use.

Furthermore, formation of nanoporous metals is being researched aiming at creating novel functional materials. In this year, we investigated the structural stability and the mechanism of annihilation of nano-pores in oxide nanoparticles, which were formed through oxidation of metal nanoparticles.

### Current Research Project

#### Development of Thermal Decomposition Method to Fabricate Lotus-type Porous Metals

We developed a novel method for fabricating lotus-type porous metals. In this method, compounds containing gas elements are thermally decomposed in liquid metal, and the decomposed gas atoms are dissolved in the liquid metal. Then, the liquid metal containing gas atoms is solidified unidirectionally. This simple procedure can achieve the fabrication of lotus metals. Porosity and pore size of lotus metals can be controlled by the amount of compounds and ambient pressure of argon gas. Fabrication of lotus

aluminum, magnesium and iron has been achieved using this method. The developed method is quite useful for mass production, because inflammable pressurized hydrogen gas is not necessary. Thus, this method will promote practical applications of lotus metals.

### **Compressive and Fatigue Properties of Lotus-type Porous Metals**

We studied the mechanical properties of lotus TiAl and lotus magnesium. The compressive yield strength of lotus TiAl decreases with decreasing porosity. It was clarified that this decrease of the yield strength is caused by local deformation around pores. The fatigue strength of lotus magnesium decreases with decreasing porosity. Fatigue fracture surface of lotus magnesium matrix is a typical fracture surface of brittle materials, and the fatigue strength is also affected by the mechanical properties of matrix.

### **Fabrication of Practical Lotus-type Porous Metals by Continuous Casting Technique**

We fabricated not only the lotus-type porous copper but also the lotus-type porous practical metals such as Al-Si alloys and carbon steel using the continuous casting technique developed for the fabrication of the lotus-type porous metal. The porosity and the pore size in the lotus-type porous metals can be controlled by the temperature of the melt, atmosphere gas pressure and the solidification velocity. This is a promising technique for low cost and mass-production for commercial application of the lotus metals and provides various products for applications such as sport utility, airplane device, heat sink, biomaterials, and machine tools, etc.

### **Development of Lotus-type Porous Ni-free Stainless Steels for Biomedical Applications**

In order to utilize the lotus-type porous stainless steel as biomedical applications, we developed the lotus-type porous Ni-free stainless steels with very small magnetic susceptibility and compressive strength close to the human cortical bone. The results of strength test, corrosion test, cell culture experiment and biocompatibility evaluation in a rat model demonstrate that the lotus-type porous Ni-free stainless steels have excellent biocompatibility.

### **Structural Stability of Hollow Oxide Nanoparticles**

Structural stability of hollow Cu and Ni oxide nanoparticles at high temperatures were studied by transmission electron microscopy. We found that annealing at high temperatures both in a vacuum and in air leads to atomic movement that results in the annihilation of nano-holes inside hollow nanoparticles, and a consequent reduction in the extra inner-surface energy

## **Publications**

### **Original Papers**

Fabrication of Lotus-type Porous Metals by Continuous Zone Melting and Continuous Casting Techniques, H. Nakajima, S.-K. Hyun, J.-S. Park, M. Tane: Mater. Sci. Forum, 539-543 (2007) 187-192.

Lotus-Type Porous Nickel-free Stainless Steel with High Temperature Nitriding, K. Alvarez, S.-K. Hyun, H. Nakajima: Mater. Sci. Forum, 539-543 (2007) 756-761.

Fabrication of Lotus-type Porous Copper-Aluminum Alloy by Unidirectional Solidification in Hydrogen Atmosphere, S.-K. Hyun, T. Awadu, T. Ikeda, H. Nakajima: Mater. Sci. Forum, 539-543 (2007) 1898-1902.

Hollow Oxide Formation via Oxidation of Al Nanoparticles at Low Temperatures, R. Nakamura, J.-G. Lee, D. Tokozakura, H. Mori, H. Nakajima: Mater. Sci. Forum, 544-545 (2007) 347-350.

Fabrication of Lotus-type Porous Ni-(15, 28 and 31) at.% Al Alloys by Unidirectional Solidification in Hydrogen Atmosphere, S.-K. Hyun, T. Ikeda, H. Nakajima: Mater. Sci. Forum, 544-545 (2007) 323-326.

Formation of Hollow ZnO through Low Temperature Oxidation of Zn Nanoparticles, R. Nakamura, J.-G. Lee, D. Tokozakura, H. Mori, H. Nakajima: Mater. Lett., 61 (4 • 5) (2007) 1060-1063.

Pore Morphology of Lotus-Type Porous Copper Fabricated by Continuous Casting Technique, J.-S. Park, S.-K. Hyun, M. Tane, H. Nakajima: Solid State Phenomena, 124-126 (2007) 1725-1728.

Fabrication of Lotus-type Porous NiAl and Ni<sub>3</sub>Al intermetallic Compounds, T. Ide, M. Tane, H. Nakajima: Solid State Phenomena, 124-126 (2007) 1721-1724.

Prediction of Laser Fusion Zone Profile lotus-type Porous Metals by 3D Heat Transfer Analysis, T. Tsumura, F. Ye, T. Murakami, H. Nakajima, K. Nakata: Solid State Phenomena, 127 (2007) 307-312.

Extended Mean-field Method for Predicting Yield Behaviors of Porous Materials, M. Tane, T. Ichitsubo, M. Hirao, H. Nakajima: Mech. Mater., 39 (1) (2007) 53-63.

Fabrication of Lotus-type Porous NiTi Shape Memory Alloys using the Continuous Zone Melting Method and Tensile Property, M. Sugiyama, S.K. Hyun, M. Tane, H. Nakajima: High Temp. Mater. Proces., 26 (4) (2007) 297-301.

Hollow Oxide Formation by Oxidation of Al and Cu Nanoparticles, R. Nakamura, D. Tokozakura, H. Nakajima, J.-G. Lee, H. Mori: J. Appl. Phys., 101 (7) (2007) 74303.

Fabrication, Properties and Application of Porous Metals with Directional Pores, H. Nakajima: Prog. Mater. Sci., 52 (7) (2007) 1091-1173.

Three-dimensinal Image-based Modeling of Lotus-type Porous Carbon Steel and Simulation of its Mechanical Behavior by Finite Element Method, T. Kujime, M. Tane,

S.-K. Hyun, H. Nakajima: Mater. Sci. Eng. A, 460-461 (2007) 220-226.

Effects of Pore Morphology on Fatigue Strength and Fracture Surface of Lotus-type Porous Copper, H. Seki, M. Tane, M. Otsuka, H. Nakajima: J. Mater. Res., 22 (7) (2007) 1331-1338.

Evaluation of Bone Quality near Metallic Implants with and without Lotus-Type Pores for Optimal Biomaterial Design, T. Ishimoto, T. Nakano, T. Kan, Y. Ohashi, W. Fujitani, Y. Umakoshi, T. Hattori, Y. Higuchi, M. Tane, and H. Nakajima: J. Jpn. Inst. Metals, 71 (4) (2007) 432-438.

Effective-Mean-Field Theory for Electrical Conductivity of Multiphase Composite Materials, M. Tane, H. Nakajima: Jpn. J. Appl. Phys, 46 (8) (2007) 5221-5225.

Anisotropic Fusion Profile and Joint Strength of Lotus-type Porous Magnesium by Laser Fusion, T. Murakami, T. Tsumura, T. Ikeda, H. Nakajima, K. Nakata: Mater. Sci. Eng. A, 456 (2007) 278-285.

Effect of transference velocity and hydrogen pressure on porosity and pore morphology of lotus-type porous copper fabricated by continuous casting technique, J.-S.Park, S.-K.Hyun, S. Suzuki, H. Nakajima: Acta Mater, 55 (16) (2007) 5646-5654.

Transmission electron microscopy observation of oxide layer growth on Cu nanoparticles and formation process of hollow oxide particles, D. Tokozakura, R. Nakamura, H. Nakajima, J.-G. Lee, H. Mori: J. Mater. Res., 22 (10) (2007) 2930-2935.

Effects of Anisotropic Pore Structure and Fiber Texture on Fatigue Properties of Lotus-type Porous Magnesium, H. Seki, M. Tane, H. Nakajima: J. Mater. Res., 22 (11) (2007) 3120-3129.

Fatigue strength of lotus-type porous magnesium, H. Seki, M. Tane, H. Nakajima: Mater. Sci. Forum, 561-565 (2007) 1681-1684.

Oxidation Behavior of Cu Nanoparticles and Formation of Hollow Cu<sub>2</sub>O Spheres, R. Nakamura, D. Tokozakura, J.-G. Lee, H. Mori, H. Nakajima: Mater. Sci. Forum, 561-565 (2007) 1703-1706.

Microstructure and Deformation Behavior of Lamellar Ti-rich TiAl Crystal with Lotus-type Aligned Pores, T. Nakano, T. Tachibana, K. Hagihara, Y. Umakoshi, T. Ide, M. Tane and H. Nakajima: Mater. Sci. Forum, 561-565 (2007) 383-386.

Laser Welding of Lotus-Type Pporous Iron, H. Yanagino, T. Tsumura, H. Nakajima, S.-K. Hyun, K. Nakata: J. Jpn. Inst. Metals, 71 (10) (2007) 896-900.

Fabrication of Lotus-type Porous Copper by Continuous Casting Technique, J.S. Park, S.K. Hyun, S.Suzuki, H.Nakajima: Journal of the JNCSu, 46 (1) (2007) 270-273.

Effects of Porosity and Pore Size Distribution on Fatigue Strength of Lotus-type Porous Copper, H. Seki, M. Tane, H. Nakajima, M. Otsuka: Journal of the JNCSu, 46 (1) (2007) 90-94.

Fabrication of Porous Copper with Directional Pores through Thermal Decomposition of Compounds, H. Nakajima, T. Ide: Metal. Mater. Trans. A, 39 (2) (2008) 390-394.

Fabrication and Mechanical Properties of Lotus-type Porous Carbon Steel by Unidirectional Solidification in Nitrogen Atmosphere, M. Kashiwara, H. Yonetani, T. Kobi, S.K. Hyun, S. Suzuki, H. Nakajima: Tetsu to hagane, 94 (1) (2008) 30-34.

Fatigue Crack Initiation and Propagation in Lotus-type Porous Copper, H. Seki, M. Tane, H. Nakajima: Mater. Trans., 49 (1) (2008) 144-150.

Oxidation Behaviour of Ni Nanoparticles and Formation Process of Hollow NiO, R. Nakamura, J.-G. Lee, H. Mori, H. Nakajima: Philos. Mag., 88 (2) (2008) 257-264.

Formation of Hollow Zinc Oxide by Oxidation and Subsequent Thermal Treatment, J.-G. Lee, R. Nakamura, D. Tokozakura, H. Nakajima, H. Mori, J.-H. Lee: Solid State Phenomena, 135 (2008) 11-14.

Fabrication of Porous Magnesium with Directional Pores through Use of Hydrogen Thermally Decomposed from MgH<sub>2</sub> Powders during Unidirectional Solidification, M. Tane, H. Nakajima: J. Mater. Res., 23 (3) (2008) 849-855.

Fabrication and Properties of Lotus-type Porous Nickel-free Stainless Steel with High Temperature Nitriding, K. Alvarez, K. Sato, S.-K. Hyun, H. Nakajima: Mater. Sci. Eng. C, 28 (1) (2008) 44-50.

Corrosion Behaviour of Lotus-type Porous High Nitrogen Nickel-free Stainless Steels, K. Alvarez, S.-K. Hyun, H. Tsuchiya, S. Fujimoto, H. Nakajima: Corro. Sci., 50 (1) (2008) 183-193.

Steady State Comparative-longitudinal Heat Flow Method Using Specimen of Different Thicknesses for Measuring Thermal Conductivity of Lotus-type Porous Metals, H. Chiba, T. Ogushi, H. Nakajima, K. Torii, T. Tomimura, F. Ono: J. Appl. Phys., 103 (1) (2008) 013515.

## **Review Papers**

Effective Elastic Constants of Lotus-type Porous Metals : Quantitative Prediction via Newly Developed Mean-field Theory, M. Tane, T. Ichitsubo, M. Hirao, and H. Nakajima: Materia, 46[2] (2007) 70-76.

Formation of Hollow Oxides via Oxidation of Metallic Nanoparticles, R. Nakamura, J.-G. Lee, H. Mori, and H. Nakajima: Catalysts&Catalysis, 49[5] (2007) 344-349.

Diffusion in TiAl Intermetallic Single Crystals, Y. Nose, T. Terashita, T. Ikeda, and H.



Nakajima: *Materia*, 46[9] (2007) 587-599.

Three-dimensional Image-based Modeling and Analysis of Lotus-type Porous Carbon Steel, T. Kujime, M. Tane, and H. Nakajima: *Materia*, 49[12] (2007) 836.

Fabrication of Lotus-type Porous Metals using Continuous Casting Technique, S. Suzuki, J.S. Park, S.K. Hyun, S.Y. Kim, M. Kashihara, H. Yonetani, and H. Nakajima, *J. High Temp. Soc.*, 34[1] (2008) 38-44.

Fatigue Strength of Lotus-type Porous Metals, H. Seki, M. Tane, and H. Nakajima, *J. High Temp. Soc.*, 34[2] (2008) 56-59.

Applications of Lotus-Type Porous Metal and Alloys for Aero Engine Components, S. Nagatome, K. Taguchi, S.K. Hyun, H. Nakajima, *J. High Temp. Soc.*, 34[2] (2008) 66-73.

### **Books**

Cellular and Porous Materials: Thermal Properties Simulation and Prediction, T. Ogushi, H. Chiba, M. Tane, and H. Nakajima, WILEY-VCH Verlag GmbH & Co. KGaA, (2008) 239-265.

Precise Control of Porous Materials and Estimation of Function and Properties, H. Nakajima, Science&Technology, (2008) 53-62.

### **Patents**

Porous Body Manufacturing Method, H. Nakajima, T. Ide, PCT/JP2007/062769

Metal Porous Body Manufacturing Method, H. Nakajima, PCT/JP2005/014731

### **International Conferences**

Electrochemical Behavior of High Nitrogen Ni-free Austenitic Stainless Steels in L929 and Cell Culture Medium, \*K. Alvarez, S.-K. Hyun, H. Nakajima, S. Fujimoto: 211th Meeting of The Electrochemical Society.

Fabrication and Functional Properties of Porous Metals with Directional Pores (invited), \*H. Nakajima: Asian Foundry Congress 2007.

Fabrication and Plastic Deformation Process of Lotus-type Porous Metals (poster), \*S. Suzuki, J.-S. Park, S.-K. Hyun, H. Utsunomiya, H. Nakajima: International Workshop for R&D Clustering among China, Japan, Korea in Eco-materials Processing (The 16th JSPS-KOSEF Core University Program (CUP) Seminar between Japan and Korea.

Mechanical Properties of Lotus-type Porous Metals (invited), H. Nakajima, \*M. Tane, S.-K. Hyun, H. Seki: International Union of Theoretical and Applied Mechanics (IUTAM) Symposium on Mechanical Properties of Cellular Materials.

Elastic, Plastic and Electrical Properties of Lotus-Type Porous Metals: Comparison with

Effective-Mean-Field and Micromechanical-Mean-Field Theories (keynote), \*M. Tane, H. Nakajima: TMS 2008 137th Annual Meeting & Exhibition.

New Fabrication Method for Lotus-Type Porous Metals and its Application (invited), \*H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Fabrication of Lotus-type Porous Carbon-steel by Continuous Casting Technique in Nitrogen Atmosphere, K. Kashiwara, \*S. Suzuki, S.-K. Hyun, H. Yonetani, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Equal-channel Angular Extrusion of Lotus-type Porous Copper, \*S. Suzuki, H. Utsunomiya, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Fabrication of Lotus-type Porous Aluminum using Moisture (poster), \*M. Tane, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Fabrication of Lotus-type Porous Magnesium using Hydrogen Desorption from  $MgH_2$  (poster), \*M. Tane, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Effects of pore size distribution and loading direction on fatigue property of lotus-type porous copper with anisotropic pore structure (poster), H. Seki, \*M. Tane, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Fabrication of Lotus-type Porous Magnesium by Continuous Casting Technique (poster), S.-K. Hyun, \*S. Suzuki, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Formation of a Nano-pore during Oxidation of Metal Nanoparticles (poster), \*R. Nakamura, D. Tokozakura, J.-G. Lee, H. Mori, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Impact Properties of Lotus-type Porous Carbon Steel Measured by Instrumented Charpy Testing (poster), \*T. Kujime, S.-K. Hyun, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Fabrication of Lotus-type Porous Al-Si by Continuous Casting Technique (poster), J.-S. Park, S.-K. Hyun, \*S. Suzuki, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Fabrication of Lotus-type Porous Nickel with Atmospheric Pressure and Foaming Agents by Mold Casting Technique, \*S.-Y. Kim, B.-Y. Hur, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Oxidation Behavior of Cu Nanoparticles and Formation of Hollow Cu<sub>2</sub>O Spheres (poster), \*R. Nakamura, D. Tokozakura, J.-G. Lee, H. Mori, H. Nakajima: The Sixth Pacific Rim International Conference on Advanced Materials and Processing (PRICM6).

Fatigue Strength of Lotus-type Porous Magnesium, H. Seki, \*M. Tane, H. Nakajima: The Sixth Pacific Rim International Conference on Advanced Materials and Processing (PRICM6).

Fabrication and Properties of Lotus-Type Porous Metals (invited), \*H. Nakajima: 9th International Symposium on Ecomaterials Processing & Design(ISEPD2008).

Fabrication of Lotus-type Porous Nickel through Thermal Decomposition Method in Ar Atmosphere (poster), \*S.-Y. Kim, H. Nakajima: 9th International Symposium on Ecomaterials Processing & Design(ISEPD2008).

Structural Stability of Hollow Oxide Nanoparticles at High Temperatures (poster), \*R. Nakamura, H. Nakajima, H. Mori: 11th Sanken, 6th Nanotechnology Center, 1st MSTEC International Symposium.

#### **Contributions to International Conferences and Journals**

|             |                                                                                                                                  |
|-------------|----------------------------------------------------------------------------------------------------------------------------------|
| H. Nakajima | Fifth International Conference on Porous Metals and Metal Foaming Technology (MetFoam2007) (International Advisory Board Member) |
| H. Nakajima | High Temperature Materials and Process (Editorial Board)                                                                         |
| H. Nakajima | High Temperature Materials and Processes (Guest Editor)                                                                          |
| H. Nakajima | Advanced Engineering Materials (Guest Editor)                                                                                    |
| H. Nakajima | Materials Transactions (Guest Editor)                                                                                            |
| H. Nakajima | Diffusion and Defect Data (Editorial Board Member)                                                                               |
| H. Nakajima | Materials Science Foundations (Editorial Board Member)                                                                           |
| H. Nakajima | Sixth Pacific Rim International Conference on Materials (PRICM-6) (Organizing Committee Member)                                  |
| H. Nakajima | International Conference on New Frontiers of Process Science and Engineering in Advanced Materials (Organizing Committee Member) |
| H. Nakajima | 4th International Conference on Diffusion in Solids and Liquids (Emeritus Organizing Committee Chairman)                         |
| H. Nakajima | International Conference on Eco-Materials Processing and Design VIII (International advisory Board Member)                       |
| H. Nakajima | 2nd International Symposium on Cellular Metals for Structural and Functional Applications (Program Committee)                    |
| H. Nakajima | International Conference on Advanced Structure and Functional Materials Design (Organizing Committee Member)                     |
| H. Nakajima | First International Conference on Light Alloy Technology and Application (Organizing Committee Member)                           |

|             |                                                                                                |
|-------------|------------------------------------------------------------------------------------------------|
| H. Nakajima | THRMEC International Conference on Advanced Materials<br>(International advisory Board Member) |
|-------------|------------------------------------------------------------------------------------------------|

### **Publications in Domestic Meetings**

|                                                         |          |
|---------------------------------------------------------|----------|
| The Japan Institute of Metals                           | 32papers |
| The Japan Institute of Light Metals                     | 3 papers |
| The Japan Copper and Copper Alloys Research Association | 1 paper  |
| Japan Heat Transfer Symposium                           | 1 paper  |
| High Temperature Society                                | 2 papers |

### **Academic Degrees**

#### **Doctor Degree for Engineering**

|            |                                                                                                            |
|------------|------------------------------------------------------------------------------------------------------------|
| T. Kujime  | Measurement and Analysis of Mechanical Properties in Lotus-type Porous Carbon Steel                        |
| J.-S. Park | Fabrication of Lotus-type Porous Copper and Al-Si Alloys by Continuous Casting Technique                   |
| T. Ide     | Fabrication and Mechanical Properties of Lotus-type Porous Stainless Steel and Intermetallic Compounds     |
| H. Onishi  | Control of Pore Morphology of Porous Nickel with Directional Pores and its Magnetic Property               |
| K. Alvarez | Fabrication and Characterization of Lotus-type Porous Ni-free Stainless Steels for Biomedical Applications |
| H. Seki    | Fatigue Properties of Lotus-type Porous Metals                                                             |

#### **Master Degree for Engineering**

|             |                                                                                                            |
|-------------|------------------------------------------------------------------------------------------------------------|
| S. Akita    | Elastic Behavior of Biomedical $\beta$ type Ti-Nb-Ta-Zr alloy                                              |
| K. Watanabe | Fabrication of Lotus-type Porous Aluminum Using Thermal Decomposition Method                               |
| T. Wada     | Fabrication of Lotus-type Porous Iron Using Thermal Decomposition Method and their Pore Morphology Control |

### **Sponsorship**

#### **Grant-in-Aid for Scientific Research (\*) (\*)**

|             |                                                                                                                       |             |
|-------------|-----------------------------------------------------------------------------------------------------------------------|-------------|
| H. Nakajima | Fabrication of Novel Nano-hollow Sphere Metals and Metallic Nano-tube and Elucidation of Physical Properties          | ¥15,470,000 |
| S. Suzuki   | Fabrication of Lotus Metals Consisting of Two Different Metals Using Continuous Casting Technique with Multiple Molds | ¥1,000,000  |
| R. Nakamura | Fabrication of Hollow Metallic Nanoparticles and Elucidation of their Formation Mechanism                             | ¥1,000,000  |

### **Entrusted Research**

|                            |                                                             |                                                                                                                                            |             |
|----------------------------|-------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| H. Nakajima                | Development of High Performance Machinery Processing System | Development of Structural Materials with Light-weight and High Stiffness and of the Estimation Method                                      | ¥23,800,000 |
| H. Nakajima                | Japan Science and Technology Agency                         | Development Project for Seeds Innovation Development of Porous Silicon Heat Sink                                                           | ¥4,893,000  |
| <b>Other Research Fund</b> |                                                             |                                                                                                                                            |             |
| H. Nakajima                | The Japan Institute of Light Metals                         |                                                                                                                                            | ¥250,000    |
| H. Nakajima                | Murayama Co.,LTD.                                           |                                                                                                                                            | ¥1,000,000  |
| H. Nakajima                | Lotus alloy Co.,LTD                                         |                                                                                                                                            | ¥1,000,000  |
| H. Nakajima                | Lotus alloy Co.,LTD                                         |                                                                                                                                            | ¥6,000,000  |
| H. Nakajima                | Myoutoku LTD.                                               |                                                                                                                                            | ¥1,000,000  |
| S. Suzuki                  | Iketani Science and Technology Foundation                   | Fabrication of Light-weight Stiff Porous Aluminum with Shock Absorption using Continuous Casting Technique and Their Mechanical Properties | ¥1,500,000  |
| R. Nakamura                | The Iron and Steel Institute of Japan                       | Formation Process of Hollow Oxides via Oxidation of Fe and Ni Nanoparticles                                                                | ¥1,500,000  |

## Department of Atomic Scale Science

|                          |                                                                                                                                                                                                                                                                         |
|--------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Professor:               | Tomoji KAWAI                                                                                                                                                                                                                                                            |
| Associate Professor:     | Hidekazu TANAKA (~H20.1.15)                                                                                                                                                                                                                                             |
| Visitor Professor:       | Hea-Yeon LEE                                                                                                                                                                                                                                                            |
| Research Associates:     | Hiroyuki TANAKA, Takeshi YANAGIDA                                                                                                                                                                                                                                       |
| Post Doctoral Fellows:   | Aurelian Marcu, Keiichi ADACHI(~H20.2.29),<br>Naoki SUZUKI, Bong-Kuk Lee, Hiroshi Matsuura,<br>Masaki KANAI, Hitomi HOKONOHARA,<br>Tomohiko TAKAMI(~H19.9.30),<br>Makusu TSUTSUI, Akihiko TAKAGI,                                                                       |
| Graduate Students:       | Koji SUZUKI, Fumihiko YAMADA,<br>Song-Eun LEE, Suguru NAKAZATO,<br>Takuya TAKAHASHI, Takumi KOBAYASHI,<br>Kazumichi YOKOTA, Kazuki NAGASHIMA,<br>Hideyuki KAWAGUCHI, Junichi TAKAOBUSHI<br>Hiroaki SAKAMOTO, Satoru YAMANAKA,<br>Kouhei SHOJI, Kazuya GOTO, Keisuke OKA |
| Under Graduate Students: | Yuji SEGAWA, Junichi NAKAGAWA,<br>Masahito KAWANO, Yautomo MORIMOTO                                                                                                                                                                                                     |
| Support Staff:           | Noriko FUJIBAYASHI, Yumi NAGAI (~H20.1.15)                                                                                                                                                                                                                              |

### Outlines

This research group directs toward both nano-science and nanobio-technology in its activity. Main subjects are (1) Preparation of Function Harmonized Artificial Lattices, (2) Atomic Scale Surface Science, (3) Development of Bio-tip, and (4) Development of bio-molecular device constructed from DNA. By use of a laser molecular beam epitaxy technique under layer by layer growth conditions, we are challenging in development of highly sensitive IR –sensor by functional transition metal oxide nano-film. Observation and manipulation of a single atom or a molecule are undertaken on DNA molecules with Scanning Probe Microscopic (SPM) methods. And also we developed the ultrasensitive electrochemical gene sensing system by using nanowell array electrodes.

### Current Research Programs and Achievements

#### Function harmonised superlattices.

- New ferromagnetic oxide, ( $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ ) was deigned and prepared to construct highly sensitive spin devices for external fields (magnetic & electric field) at room temperature.
- At the thickness around 40nm, the  $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$  thin films possessed high TCR value and low noise amplitude at room temperature, showing higher potential as an uncooled bolometer than the ordinary VO<sub>x</sub>-based IR sensor.
- The ultimate nano-lithography for various kinds of transition metal oxide films has achieved down to 30nm using atomic force microscopy.
- Oxide heteronanowires have been fabricated, which allow us to fabricate arbitrary

any transition metal oxides into nanowire structures.

#### **Nano-science by using of Scanning Probe Microscopes.**

- By using scanning tunneling microscopy (STM), we obtained submolecular-resolution STM images of a single molecule of DNA labeled with a fluorophore, such as FITC, RITC, HEX, etc., which can be a good molecular marker even in STM.
- By using STM/STS measurements, a characteristic peak in  $dI/dV$  spectra of Guanine molecule has been detected.
- Using the atomic force microscopy (AFM), we found the valuable information to identify the solution for the rate-limiting step of small-scale protein synthesis system by analyzing the reaction process.
- Using the base recognition function of the immobilized ribosome, the base sequencing process of mRNA was detectable with the optical technique, which did not need any special purifications.

#### **Development of NanoBiosensor**

- Developing ultra-sensitive biosensor/devices utilizing highly-specific bindings on nano-sized electrode arrays.
- Development of novel bio-sensor was achieved by coordinating functional groups on the surface of lipid-bilayer.

#### **Development of bio-molecular device constructed from DNA.**

- DNA nano-patterning by a nanoimprint lithography (NIL) and novel patterning technique toward DNA electronic nano devices were developed.
- One dimensional gold particle array have been formed using DNA template.
- Nano-scale gold electrodes have been fabricated by using nanotransfer printing lithography.
- Direct detection of the known SNPs (single nucleic polymorphism) of Cytochrome P450 2C9 (CYP2C9), which is a polymorphic enzyme responsible for the metabolism of a large number of clinically important drugs in the Cytochrome P450 superfamily, using a PNA-modified IS-FET biosensor.

### **Publications**

#### **Original Papers**

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Single Probe DNA Immobilization on Chemically Modified Single Protein by controlling Ionic Strength and PH, R.Yamazaki, M.Ito, B.K.Lee, H.S.Jung, H.Y.Lee, T.Kawai: *Analytica Chimica Acta*, 603 (2007) 76-81.

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Thickness Dependence of Structure and Magnetization of BiFeO<sub>3</sub> Films on (LaAlO<sub>3</sub>)<sub>0.3</sub>(Sr<sub>2</sub>AlTaO<sub>6</sub>)<sub>0.7</sub> (001) Substrate, Rana, D.S., K.Takahashi, K.R.Mavani, I.Kawayama, H.Murakami, M.Tonouchi, T.Yanagida, H.Tanaka and T.Kawai: Phys. Rev. B, 75 (2007) 60405.

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Control of the Electrode-Molecule Interface for Molecular Devices, K. Yokota, M. Taniguchi, T. Kawai: J. Am. Chem. Soc., 129 (2007) 5818-5819.

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Tunnelling Charge Injection into a Pentacene Layer Using Dynamic-Mode Scanning Force Microscopy, T. Kusaka, K. Ojima, T. Matsumoto and T. Kawai: Nanotechnology, 18 (2007) 95503.

Discrete Dihedral-Angle Modulation in Porphyrin Wheels Adsorbed on Cu(100) Observed by Scanning Tunneling Microscopy, A. Takagi, T. Hori, X. Peng, N. Aratani, T. Matsumoto, A. Osuka and T. Kawai: Surf. Sci., 601 (2007) 2178-2181.

Dielectric Properties of Ba(Zr, Ti)O<sub>3</sub> Thin Films Fabricated by Pulsed Laser Deposition, Takanori Hino, Minoru Nishida, Takao Araki, Takahiro Ohno, Toshio Kawahara, Masakazu Murasugi, Hitoshi Tabata and Tomoji Kawai: Journal of Laser

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Possibility of reverse Monte Carlo modelling for hydrogenated amorphous Si deposited on reactive ion etched Si substrate, Toshio Kawahara, Yoshinori Matsui, Seiichi Tagawa, Tomoji Kawai and Hideki Matsumura: J. Phys.: Condens. Matter, 19 (2007) 335211.

### **Review Papers**

Development of nano-molecular device via self-organized wiring method, Masateru Taniguchi, Tomoji Kawai, Nano Gakkai Kaihou, 6 (2006) 23-28.

Physical Origin of electron-doped manganese oxides, Takeshi Yanagida, Hidekazu Tanaka, Tomoji Kawai, Osaka University Teion Center Dayori, 139 (2007) 9-14.

### **Books**

Scanning Probe Microscopy, in The Fifth Series of Experimental Chemistry, vol. 28, Nanotechnology Chemistry, Takuya Matsumoto, Maruzen, (2005) 133-165

Analysis of Organic and Biological Molecules, in Scanning Probe Spectroscopy for Nanoscale Science and Technology, T. Matsumoto, T. Kawai, ed. By H. Shigekawa, M. Yoshimura, M. Sakata, A. Kawazu, Shokabo (2005) 371-388

### **Patents**

Probe Device, Takuya Matsumoto, Yasuhisa Naitoh, Tomoji Kawai, US 7,250,302 B2, 2007/07/31

Fabrication method and substrate preparation for single DNA molecules, Tomohide Takami, Hiroyuki Tanaka, 2007-196620, 2007/07/27

### **International Conference**

Programmed Self-organization for NanoBio-devices (invited), Tomoji KAWAI: 8th International Symposium on Biomimetic Materials Processing.

Nano-Structured Functional Oxides (invited), Tomoji KAWAI: International Conference on Nano and Microelectronics (ICONAME-2008).

Nano-structured functional oxides (invited), Tomoji KAWAI: 7th France-Japan Workshop on Nanosciences and Nanomaterials.

Nano-structured Functional Oxides (poster), Kawai, T., H. Tanaka, T. Yanagida, N. Suzuki, S. Yamanaka, Y. Yanagisawa, K. Nagashima and A. Marcu: The 14th International Workshop on Oxide Electronics.

High resolution imaging and spectroscopy of DNA by STM/STS (invited), Tomoji KAWAI: Colloquium Spectroscopicum Internationale XXXV.

DNA Nanotechnology toward Future Nanoelectronics (invited), Tomoji KAWAI: Osaka Univ./LANL International Workshop.

Nanoscience and Nanotechnology in Japan and Kawai Laboratory (invited), Tomoji KAWAI: The First Thailand National Nanotechnology Conference.

Nano-structured biosensors –An integrated digital biosensor with functional vesicle using oriented nanoWell array electrode (invited), Tomoji KAWAI: IVC-17/ICSS-13 and ICN+T2007.

SPM for nanobio-science and technology –single-nucleotide detection of DNA base molecules- (invited), Tomoji KAWAI: JEJU 2007 ISPM (International Scanning Probe Microscopy Conference).

Inelastic tunneling spectroscopy of single molecule using nanofabricated mechanically controllable break-junction (invited), M. Taniguchi, M. Tsutsui, K. Shoji, T. Kawai,: CREST Symposium on Theories and Simulations for Charge Migration and Chemical Reactions at Nano-Scale Interfaces.

Self-organized interconnect method for molecular devices (invited), M. Taniguchi, Jun Terao, and Tomoji Kawai: CREST-Nanolink joint international workshop on “Electron transport through a linked molecule in nano-scale”.

Toward Digital NanoBioCHIP (invited), H.Y.Lee, B.K.Lee, T.Kawai: Invited Seminar, Department of veterinary and biomedical science, Penn State Neuroscience Institute.

Well-Oriented NanoWell Array Metrics for Digital NanoBioChip (poster), H.Y.Lee, B.K.Lee, T.Kawai: APS-March Conference.

Integrated Biocompatible Nanobiochip (invited), H.Y.Lee, B.K.Lee, T.Kawai: The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science.

NanoWell based Electrochemical NanobioCHIP toward mult-Nanomedicine (invited), H.Y.Lee, B.K.Lee, T.Kawai: The 6th Japan-Korea Nanotech Industrialization Forum.

Biocompatible NanoWell Geometry-BioCHIP toward Digital Analysis (poster), H.Y.Lee, B.K.Lee, T.Kawai: 11th Sanken International Symposium.

Integrated Electronic-Nanowell BioCHIP (poster), H.Y.Lee, B.K.Lee, T.Kawai: The 1st Global COE International Symposium- Electronic Devices Innovation - (EDIS2008).

Facile and Rapid Direct Gold Surface Immobilization with Controlled Orientation for Carbohydrates (poster), J.H.Seo, K.Adachi, B.K.Lee, D.G.Kang, Y.K.Kim, K.R.Kim, H.Y.Lee, T.Kawai, H.J.Choa: The 1st Global COE International Symposium- Electronic Devices Innovation - (EDIS2008).

Integrated Electric NanobiosensorCHIP (invited), H.Y.Lee, B.K.Lee, T.Kawai: Plenary talk, Korea-MRS.

NanoWell Geometry-BioCHIP toward Single Molecular Analysis (invited), H.Y.Lee, B.K.Lee, T.Kawai: Biochemical Engineering of Korea.

Nanoarray of Tethered Bilayer Lipid Membrane (tBLM)-Formed Lipid Rafts with a Nanoimprinted Poly(Vinyl Alcohol) Hydrogel (invited), B.K.Lee, H.Y.Lee, T.Kawai: Biochemical Engineering of Korea.

Self-assembled biomolecule nanoarray for electronic biochips (invited), H.Y.Lee: The 3rd Nanoelectronics and Dynamics of DNA.

Self-organized Functional Lipid Vesicle Array for Sensitive Immunoassay chip (invited), H.Y.Lee, T.Kawai: ISPM (International Scanning Probe Microscopy) conference.

Surface Potential and Capacitance Images of Biological Molecules on Insulating Substrates (poster), T. Matsumoto, F. Yamada, E. Mikamo-Sato, A. Takagi, T. Kawai: 10<sup>th</sup> International Non-Contact AFM 2007.

Molecule Recognition Imaging by Frequency Shift Detection in Liquid (poster), T. Matsumoto, T. Kawahara, H. Hokonohara, T. Kawai: 10<sup>th</sup> International Non-Contact AFM 2007.

Surface Potential and Capacitance Images of Biological Molecules on Insulating Substrates (poster), T. Matsumoto, F. Yamada, E. Mikamo-Sato, A. Takagi, T. Kawai: 15th International Colloquium on Scanning Probe Microscopy (ICSPM15).

Nanowire Heterostructures of Transition Metal Oxides (poster), Yanagida, T., K.Nagashima, A.Marcu, K.Oka, H.Tanaka and T.Kawai: 14th International Workshop on Oxide Electronics.

Heterostructures of Transition Metal Oxide Nanowires (poster), Yanagida, T., K.Nagashima, A.Marcu, K.Oka, H.Tanaka and T.Kawai: Material Research Society Fall Meeting.

Nature of Transport Properties in Low Temperature Grown NiO films (poster), Oka, K., T.Yanagida, K.Nagashima, H.Tanaka and T.Kawai: 15th International Colloquium on Scanning Probe Microscopy.

Role of Three Dimensional Epitaxy on MgO/NiO Heterostructured Oxide Nanowire Formation (poster), Oka, K., T.Yanagida, K.Nagashima, H.Tanaka and T.Kawai: 15th International Colloquium on Scanning Probe Microscopy.

Effect of Heterointerface on Transport Properties of In-situ Formed MgO/titanate Core-shell Nanowires (poster), Oka, K., K.Nagashima, T.Yanagida, H.Tanaka and T.Kawai: 15th International Colloquium on Scanning Probe Microscopy.

Crucial role of heterointerface on MgO/titanate core-shell nanowires (poster),

Nagashima, K., T.Yanagida, K.Oka, H.Tanaka, S.Seki, A.Saeki, S.Tagawa and T.Kawai: 1st Global COE International Symposium Electronic Devices Innovation.

Significance of 3D Epitaxy on Heterostructured Oxide Nanowires (poster), Oka, K., T.Yanagida, K.Nagashima, H.Tanaka and T.Kawai: 1st Global COE International Symposium Electronic Devices Innovation.

Transport Nature of Low Temperature Grown NiO Thin Films (poster), Oka, K., T.Yanagida, K.Nagashima, H.Tanaka and T.Kawai: 11th Sanken, 6th Nanotechnology Center and 1st MSTEC International Symposium New Advances in Nanoscience & Nanotechnology.

In-situ Formation of MgO/NiO Heterostructured Oxide Nanowires (poster), Oka, K., T.Yanagida, K.Nagashima, H.Tanaka and T.Kawai: 11th Sanken, 6th Nanotechnology Center and 1st MSTEC International Symposium New Advances in Nanoscience & Nanotechnology.

Crucial Role of Heterointerface on Transport Properties of In-situ Formed MgO/titanate Core-Shell Nanowires (poster), Oka, K., T.Yanagida, K.Nagashima, H.Tanaka and T.Kawai: 11th Sanken, 6th Nanotechnology Center and 1st MSTEC International Symposium New Advances in Nanoscience & Nanotechnology.

Fabrication of Heterostructured Oxide Nanowires and Effect of Heterointerface on the Transport and Magnetic Properties (invited), Yanagida, T., K.Nagashima, K.Oka, H.Tanaka and T.Kawai: Workshop on SAKURA Project.

Heterostructured Oxide Nanowires (poster), Yanagida, T., K.Nagashima, K.Oka, H.Tanaka and T.Kawai: The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science.

Size and distribution control of Co nano clusters grown by arc plasma gun (poster), \*Toshio Kawahara, Teruo Kanki, Yasushi Hotta, Naoki Asakawa, Tomoji Kawai, Hitoshi Tabata: 9th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN9), Tokyo, Japan, Nov. 11-15, 2007.

Magneto-Electric Properties of Photoinduced Magnet (Al,Ru,Fe)O<sub>3</sub> Thin Films (poster), \*T.Kanki, Y.Hotta, N.Asakawa, T.Kawahara, H.Tabata, T.Kawai: The 14th. International Workshop on Oxide Electronics.

Epitaxial growth of spinel ferrite oxide (Al,Ru,Fe)<sub>3</sub>O<sub>4</sub> on a GaAs(001) substrate using a MgO buffer layer (poster), \*T.Kanki, T.Kawahara, N.Asakawa, Y.Hotta, Y.Terai, Y.Fujiwara, H.Tabata, T.Kawai: 2007 MRS fall meeting.

### **Contributions to International Conferences and Journals**

Tomoji Kawai    Nanotech (Chairman)

Tomoji Kawai    Surface Science (Editorial Board)

**Publications in Domestic Meetings**

|                                        |           |
|----------------------------------------|-----------|
| The Physical Society of Japan          | 7 papers  |
| The Japan Society of Applied Physics   | 21 papers |
| The Chemical Society of Japan          | 3 papers  |
| The Molecular Biology Society of Japan | 1 paper   |
| Others                                 | 11 papers |

**Academic Degrees****Doctor Degree of Engineering Science**

|          |                                                                                                           |
|----------|-----------------------------------------------------------------------------------------------------------|
| F.Yamada | Studies on nanoscale electrical and magnetic properties of DNA complexes with nanoparticles and molecules |
|----------|-----------------------------------------------------------------------------------------------------------|

**Master Degree of Science**

|            |                                                                                                   |
|------------|---------------------------------------------------------------------------------------------------|
| H.Sakamoto | Extension of DNA polymer and STM/STS of structure and electronic states of individual nucleotides |
|------------|---------------------------------------------------------------------------------------------------|

**Master Degree of Life Science**

|             |                                                                                |
|-------------|--------------------------------------------------------------------------------|
| T.Kobayashi | Polysome analysis of translation process in cell-free protein synthesis system |
|-------------|--------------------------------------------------------------------------------|

**Master Degree of Engineering Science**

|              |                                                                                                                                                                                    |
|--------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| H.Kawaguchi  | Effect of insulating layer on ambipolar organic field effect transistor                                                                                                            |
| K.Nagashima  | Synthesis and characterization of transition metal oxide nano-structures toward room temperature operating devices                                                                 |
| J.Takaobushi | Preparation of (Fe,Zn) <sub>3</sub> O <sub>4</sub> thin films as a magnetic semiconductor with strongly correlated electron system and application to the field effect spin device |

**Sponsorship****Grant-in-Aid for Scientific Research (A)**

|          |                                                           |             |
|----------|-----------------------------------------------------------|-------------|
| T. Kawai | Study on fabrication and properties of DNA nanostructures | ¥15,600,000 |
|----------|-----------------------------------------------------------|-------------|

**Grant-in-Aid for Young Research (B)**

|             |                                                      |            |
|-------------|------------------------------------------------------|------------|
| T. Yanagida | Properties and fabrication of transition metal oxide | ¥2,100,000 |
|-------------|------------------------------------------------------|------------|

nanowires

**Fund for JSPS Research fellowships for Young Scientist**

|            |                                                                                            |            |
|------------|--------------------------------------------------------------------------------------------|------------|
| A.Marcu    | Mechanism of oxide thin film growth by pulsed laser deposition toward functional materials | ¥1,200,000 |
| M. Tsutsui | Study on photo-switching of single organic molecule by MCBJ method                         | ¥1,200,000 |

**Entrusted Research**

|          |               |                                                          |            |
|----------|---------------|----------------------------------------------------------|------------|
| T. Kawai | NEDO project  | Research and Development of High Through Put Bio Chip    | ¥6,432,000 |
| T. Kawai | Sysmex co.    | Study of high-sensitivity biosensor using nano-electrode | ¥7,772,000 |
| T. Kawai | Panasonic co. | Study on molecular device                                | ¥1,968,000 |

**Other Research Funds**

|             |                                                                                                   |                                                                                                        |              |
|-------------|---------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|--------------|
| T. Kawai    | Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency | Creation of bio-mimetic intellectual material based on programmed self-assembly                        | ¥109,500,000 |
| T. Kawai    | Nanotechnology Researchers Network Center of Japan                                                | Nanotechnology Process Foundry                                                                         | ¥103,000,000 |
| T. Kawai    | Creation of Advanced Innovation Center                                                            | Intelligent Artificial devices and Information Systems                                                 | ¥78,530,000  |
| T. Yanagida | Japan Science and Technology Agency                                                               | Seed Excavation Funds- Development of nonvolatile memory device using transition metal oxide nanowires | ¥2,000,000   |
| T. Yanagida | JSPS SAKURA Project                                                                               | Study on dynamic strain in transition metal oxides                                                     | ¥1,000,000   |

## Department of Functional Ceramic Materials

|                            |                                                                                                                   |
|----------------------------|-------------------------------------------------------------------------------------------------------------------|
| Professor:                 | Hikaru KOBAYASHI                                                                                                  |
| Associate Professor:       | Masao TAKAHASHI                                                                                                   |
| Research Associates:       | Kohji NOBUGAI, Taketoshi MATSUMOTO                                                                                |
| Visiting Professors:       | Hitoo IWASA, Sumio TERAOKA, Yoshihiro NAKATO                                                                      |
| Research Technical Expert: | Masami SHOJI                                                                                                      |
| Researchers:               | Yueh-Ling LIU, Mikihiro YAMADA, Toru YOSHIDA                                                                      |
| Graduate Students:         | Yukio ISHIKAWA, Mohammad MADANI, Kentaro IMAMURA, Masahide URAGOU, Takeru SHISHIDO, Takashi IWATA, Takashi YANASE |
| Undergraduates:            | Yuko Higashi                                                                                                      |
| Support Staff:             | Chika KUROSAKI, Reiko NOZAKURA                                                                                    |

### Outlines

The modern society is based on semiconductor technology. Our research is aiming to improve the characteristics of semiconductor devices and to develop semiconductor devices with new structures. For this purpose, we have developed new semiconductor chemical processes such as low temperature Si oxidation method by use of nitric acid and room temperature defect passivation method. Semiconductor devices studied in this department are: 1) Si solar cells, 2) Si or SiC-based metal-oxide-semiconductor (MOS) devices for LSI, 3) thin film transistors (TFT) for display devices.

### Current Research Project

#### Low Temperature Fabrication of Thick SiO<sub>2</sub>/Si and SiO<sub>2</sub>/SiC Structures by Use of Chemical Method and its Application to Thin Film Transistors (TFT)

TFT is fabricated by the deposition of SiO<sub>2</sub> layers using a CVD method on polycrystalline Si thin films deposited on glass substrates. Due to the use of glass substrates, thermal oxidation which requires heat treatments at above 800 °C cannot be employed. SiO<sub>2</sub> layers formed by deposition methods possess poor characteristics, and moreover, it is impossible to form SiO<sub>2</sub> layers with uniform thickness on rough polycrystalline Si surfaces. Consequently, the formation of thick SiO<sub>2</sub> layers of ~50 nm thickness is required to achieve sufficiently low leakage current densities. Moreover, the interfacial characteristics of deposited SiO<sub>2</sub> layers are poor, resulting in a decrease in the mobility. Due to the large SiO<sub>2</sub> thickness, the electricity consumption for the TFT operation increases.

We have developed a low temperature formation method of thick SiO<sub>2</sub> layers by use of “two-step nitric acid oxidation method”. This method consists of the first immersion of Si in ~40% nitric acid solutions and the second immersion in 68% nitric acid (i.e., azeotropic mixture of nitric acid with water). Using this two-step nitric acid oxidation method, we have succeeded in the formation of SiO<sub>2</sub> layers with thickness more than 20 nm at ~120 °C. The SiO<sub>2</sub> layers formed by the first immersion possess nano-size pores, and nitric acid is decomposed at the nano-size pores during the second



immersion, leading to the generation of dissociated oxygen ions ( $O^-$ ) with high oxidizing activity. The  $SiO_2/Si$  structure fabricated by use of the two-step nitric acid oxidation method possesses much superior electrical characteristics to those formed by CVD methods.  $SiO_2$  layers formed by the two-step nitric acid oxidation method can be applied to gate oxide layers in TFT. Since the nitric acid oxidation is a direct oxidation method,  $SiO_2$  layers with a uniform thickness can be formed even on rough surfaces, and moreover, excellent interfacial characteristics can be obtained, leading to lowering of electricity consumption for the TFT operation and improvement of TFT characteristics. Moreover, flexible TFT can be achieved by employing polymer substrates such as PET since  $SiO_2$  layers can be formed at low temperature of  $\sim 120^\circ C$  by use of the two-step nitric acid oxidation method.

We have improved an apparatus for nitric acid oxidation of poly-Si deposited on glass substrates with  $30 \times 42 \text{ cm}^2$  in size for TFT. The surface concentration of metal contaminants was less than  $3 \times 10^9 \text{ atoms/cm}^2$  (i.e., lower limitation of detection for total reflection X-ray fluorescence) which is sufficiently low for LSI (Large Scale Integration) fabrication. Using this apparatus, NAOS treatment for short time becomes possible because samples can be immersed in boiling  $HNO_3$ .

We have also characterized  $SiO_2$  films on 3C-SiC surfaces formed by NAOS. SiC is known as compounds with wide band-gaps and good thermal conductivity suitable for power devices. SiC high-frequency devices are also expected because electron mobilities of SiC are much higher than that of Si. However, SiC MOS transistors with thermal oxide films show poor electrical characteristics due to accumulation of graphitic carbon at the SiC- $SiO_2$  interface. Two step NAOS can form a thick (e.g. 10 nm) and smooth  $SiO_2$  layer on a 3C-SiC surface after heat treatment at  $400^\circ C$  in pure hydrogen to flatten the SiC surface. The leakage current density was sufficiently low to use as insulating films for SiC MOS transistors.

### **Development of Semiconductor Defect Passivation Etch-Less Cleaning Method by Use of a New Chemical Reaction**

We have developed the “semiconductor defect passivation etch-less cleaning method”. Metal contaminants on semiconductor surfaces are removed by the direct reaction of the developed semiconductor cleaning solution with metal contaminants to form stable complex ions. Consequently, re-adsorption of metal species in the cleaning solution does not occur, resulting in the complete removal of metal contaminants to the surface concentration below  $10^9 \text{ atoms/cm}^2$  order. Due to the great cleaning ability of the solution, the semiconductor cleaning can be performed at room temperature (cf. conventional cleaning solutions:  $50 \sim 80^\circ C$ ), and moreover, the cleaning solutions even with concentration as low as 0.02 % possess sufficiently high cleaning ability. Furthermore, defect states such as Si dangling bonds are passivated by the cleaning solutions, leading to improvements of characteristics of semiconductor devices such as LSI, TFT, and solar cells.

We have proved that the developed semiconductor cleaning solutions can remove various kinds of metal contaminants such as Cu, Ni, Fe, Co, Mn, Zn, Ca, and Na from  $SiO_2$  and Si surfaces. The mechanism of the Ni removal from the  $SiO_2$  surfaces has been clarified. Ni contaminants on the  $SiO_2$  surface are present as  $SiO-NiOH$ . The removal mechanism consists of 2 steps. The fast and slow processes are attributed to the removal of  $SiO-NiOH$  on terraces and in sub-nanometer pores, respectively. The

cleaning ability of the HCN aqueous solutions is much better than  $\text{NH}_3$  aqueous solutions, because of high reactivity to form Ni-cyanide complex ions and avoidance of re-adsorption of  $\text{Ni}(\text{CN})_4^{2-}$  complex ions in the solutions.

### **Fabrication of solar cells with light trapping system**

The development of high-efficiency a-Si:H solar cells has been achieved by fabrication of the light trapping structures with  $\text{Al}_2\text{O}_3$  fine particles. As a result of inserting the  $\text{Al}_2\text{O}_3$  fine particles between the a-Si:H and the Ag back electrodes, the remarkable increase in the short circuit photocurrent density was achieved, while no significant change was observed both in the open circuit voltage and the fill factor. Observation of quantum efficiency spectra for the solar cells with  $\text{Al}_2\text{O}_3$  particles indicated that this increase in the photocurrent density is due to the improvement of the photo-sensitivity in the long wavelength regime (570-750 nm). It is concluded that  $\text{Al}_2\text{O}_3$  particles cause random reflection of the incident light at the interface, leading to an increase in the optical path.

## **Publications**

### **Original Papers**

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Nitric Acid Oxidation Method to Form  $\text{SiO}_2$ /3C-SiC Structure at 120 °C, S.-S. Im, S. Terakawa, H. Iwasa and H. Kobayashi: Appl. Surf. Sci., 254 (12) (2008) 3667-3671.

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### **Patents**

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Methods and apparatuses of formation of insulating films, production of semiconductor apparatuses, semiconductor apparatuses and, treatment methods of SiC surfaces, H. Kobayashi: PCT/JP2007/64759.

Methods and apparatuses of formation of insulating films, production of semiconductor apparatuses, H. Kobayashi, 4095615 (Tokugan 2005-039721).

Cleaning methods of semiconductor apparatuses, production methods of cleaning solution, cleaning methods of apparatuses to produce semiconductor apparatuses, and cleaning methods, H. Kobayashi, TBA (Tokugan2004-092281).

### **International Conferences**

Nitric Acid Oxidation of Si and SiC for the Low Temperature Fabrication of MOS Structure (invited), H. Kobayashi, Asuha, T. Matsumoto and M. Takahashi: Interntional Seminar on Semiconductor Surface Passivation 2007.

Surface Chemistry in Si Cleaning with Cyanides Solutions (invited), M. Takahashi, Y.-L. Liu and H. Kobayashi: Interntional Seminar on Semiconductor Surface Passivation 2007.

On Formation and Passivation of Defect States in Si- and GaAs-Based Semiconductor Structures (invited), E. Pincik, H. Kobayashi, R. Brunner, M. Takahashi, Y.-L. Liu, K. Imamura and J. Rusnak: Interntional Seminar on Semiconductor Surface Passivation 2007.

New Advanced Charge Version of Deep Level Transient Spectroscopy Equipment and Its Application at Investigation of Passivated Very Thin Oxide/Silicon Structures (poster), J. Rusnak, E. Pincik, M. Takahashi, R. Brunner and M. Ruzinsky: Interntional Seminar on Semiconductor Surface Passivation 2007.

Photoluminescence of Passivated a-Si:H (poster), R. Brunner, E. Pincik, H. Kobayashi, M. Takahashi, M. Kucera and J. Rusnak: Interntional Seminar on Semiconductor

Surface Passivation 2007.

Nitric Acid Oxidation of Si (NAOS) and Defect Passivation Etch-Less Cleaning (DPEL) Method to Improve Si Devices (poster), T. Matsumoto, Asuha, Y.-L. Liu, S. Imai, S. Mizushima, M. Takahashi, and H. Kobayashi: 3rd Handai Nano Symposium.

Nitric Acid Oxidation of SiC for Fabrication of 3C-SiC Based MOS Deveices (poster), H. Kobayashi, S. Im, M. Takahashi and H. Nagasawa: International Conference on Silicon Carbide and Related Materials 2007.

Removal of Copper Adsorbate from Silicon Surfaces by the use of Semiconductor Cleaning Solutions with Capability of Defect Passivation (poster), M. Takahashi, H. Narita, T. Shishido, H. Iwasa and H. Kobayashi: 11th Sanken, 6th Nanotechnology Center and 1st MSTEC Internationa Symposium.

### **Contributions to International Conferences and Journals**

|              |                                        |
|--------------|----------------------------------------|
| H. Kobayashi | Applied Surface Science (Editor)       |
| M. Takahashi | Applied Surface Science (Guest Editor) |

### **Publications in Domestic Meetings**

|                                      |          |
|--------------------------------------|----------|
| The Physical Society of Japan        | 2 papers |
| The Japan Society of Applied Physics | 7 papers |
| The Surface Science Society of Japan | 2 papers |
| Surface and Interface Spectroscopy   | 1 paper  |

### **Academic Degrees**

#### **Master Degree for Science**

|             |                                                                                                                                                                               |
|-------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| K. Imamura  | Study on formation mechanism and application to gate insulator of SiO <sub>2</sub> film formed by nitric acid                                                                 |
| M. Urago    | Physical and electronic characterization of SiO <sub>2</sub> films formed on poly-Si surfaces by nitric acid oxidation at low temperature                                     |
| T. Shishido | Characterization of photoelectric conversion properties of single crystalline solar cells: measurement of local photovoltage and observation of structures of Si/Al interface |

### **Sponsorship**

#### **Entrusted Research**

|              |                                     |                                                                                                                    |             |
|--------------|-------------------------------------|--------------------------------------------------------------------------------------------------------------------|-------------|
| H. Kobayashi | Japan Science and Technology Agency | Low temperature formation of TFT gate oxide layers and lower power consumption by the nitric acid oxidation method | ¥74,100,000 |
|--------------|-------------------------------------|--------------------------------------------------------------------------------------------------------------------|-------------|

|              |                                           |                                                                                                                                     |            |
|--------------|-------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|------------|
| H. Kobayashi | Japan Science and Technology Organization | Mechanism of new defect passivation method and low temperature oxidation method and the application of their methods to solar cells | ¥2,500,000 |
| M. Takahashi | Japan Science and Technology Agency       | Cyanide treatment of polycrystalline silicon thin films and decrease in carrier recombination                                       | ¥6,240,000 |

## Department of Frontier Materials Creation

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Supporting Staff: Rie SUEHIRO

### Outlines

The research of the Department of Frontier Materials Creation focuses on growths of high-quality single crystals and top-notch transport measurements of novel materials, such as high-temperature superconductors or spin Hall insulators. Our emphasis is on precise and systematic measurements of basic physical properties, which allows one to unveil the peculiar electronic states of novel materials. This is achieved by combining the expertise in solid-state physics and applied chemistry. Our goal is two-fold: Creating innovative materials for solving urgent issues of the human society, while exploring fundamental new physics in condensed matter.

### Current Research Project

#### Basic Research of High-Tc Superconductors

The mechanism of the high-Tc superconductivity remains one of the most challenging problems in modern condensed-matter physics. This project focuses on the physics of the high-Tc cuprate materials to understand why superconductivity occurs in these materials at notably high temperatures, the answer to which might help us find a blueprint for “room-temperature” superconductors. To elucidate the mechanism of the high-Tc superconductivity, it is important to understand the normal state from which the superconductivity emerges, because it has turned out that the “normal” state of the cuprate materials is actually quite anomalous, while the superconducting state appears to be rather ordinary except for the d-wave nature of the gap. Since the peculiarity of the normal state is strongly manifested in the transport properties (such as the temperature dependences of the resistivity and the Hall coefficient), measurements of various transport properties are essential for the high-Tc research. In the Department of Frontier Materials Creation, we therefore conduct high-accuracy measurements of the anisotropic resistivity, magnetoresistance, Hall coefficient, thermal conductivity, and thermopower; to corroborate those transport measurements, we also measure the magnetic susceptibility and specific heat, covering most of the basic material properties. Furthermore, we devote a lot of effort to growing high-quality single crystals of various

cuprate materials. The crystals are used for our own transport measurements as well as for various other measurements (ARPES, STM, optics, neutron scattering, Raman spectroscopy, etc.) through world-wide collaborations. The in-house crystal growths are very important for our own transport properties research, because systematic controls of various parameters (such as carrier concentration, impurity concentration, and chemical pressure) are indispensable for deducing useful information from the transport data.

### **Basic Research of Spin-Hall Insulators**

This project explores new avenues of the spintronics to utilize the intrinsic and dissipationless spin current that is expected to flow in spin Hall insulators. This is quite a different approach from the mainstream spintronics research to utilize magnetic materials or conventional semiconductors, where energy dissipation is inevitable. The idea of the spin Hall insulator was theoretically proposed a few years ago but is yet to be experimentally confirmed, so the primary objective of this project is to detect the intrinsic spin currents in candidate insulators. In addition, we investigate the nature of quantum spin Hall insulator, which is expected to be a new state of matter with quantized surface spin currents, while exploring ways to utilize intrinsic spin currents for spintronics applications. To take advantage of our expertise, this project will focus on clean bulk samples, which makes it distinguished from many other projects that are based on thin films.

### **Publications**

#### **Original Papers**

Visualizing pair formation on the atomic scale in the high-T<sub>c</sub> superconductor Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+d</sub>, K. K. Gomes, A. N. Pasupathy, A. Pushp, S. Ono, Y. Ando and A. Yazdani: *Nature*, 447 (7144) (2007) 569-572.

Hierarchy of multiple many-body interaction scales in high-temperature superconductors, W. Meevasana, X. J. Zhou, S. Sahrakorpi, W. S. Lee, W. L. Yang, K. Tanaka, N. Mannella, T. Yoshida, D. H. Lu, Y. L. Chen, R. H. He, H. Lin, S. Komiya, Y. Ando, F. Zhou, W. X. Ti, J. W. Xiong, Z. X. Zhao, T. Sasagawa, T. Kakeshita, K. Fujita, S. Uchida, H. Eisaki, A. Fujimori, Z. Hussain, R. S. Markiewicz, A. Bansil, N. Nagaosa, J. Zaanen, T. P. Devereaux and Z. X. Shen: *Phys. Rev. B*, 75 (17) (2007) 174506/1-7.

Low-energy electronic structure of the high-T<sub>c</sub> cuprates La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> studied by angle-resolved photoemission spectroscopy, T. Yoshida, X. J. Zhou, D. H. Lu, S. Komiya, Y. Ando, H. Eisaki, T. Kakeshita, S. Uchida, Z. Hussain, Z. X. Shen and A. Fujimori: *J. Phys.-Condens. Matter*, 19 (12) (2007) 125209/1-23.

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Microscopic annealing process and its impact on superconductivity in  $T'$ -structure electron-doped copper oxides, H. J. Kang, P. C. Dai, B. J. Campbell, P. J. Chupas, S. Rosenkranz, P. L. Lee, Q. Z. Huang, S. L. Li, S. Komiya and Y. Ando: *Nat. Mater.*, 6 (3) (2007) 224-229.

Muon spin relaxation study of superconducting  $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+d}$ , P. L. Russo, C. R. Wiebe, Y. J. Uemura, A. T. Savici, G. J. MacDougall, J. Rodriguez, G. M. Luke, N. Kaneko, H. Eisaki, M. Greven, O. P. Vajk, S. Ono, Y. Ando, K. Fujita, K. M. Kojima and S. Uchida: *Phys. Rev. B*, 75 (5) (2007) 54511/1-14.

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Observation of a 500 meV collective mode in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{Nd}_2\text{CuO}_4$  using resonant inelastic x-ray scattering, J. P. Hill, G. Blumberg, Y. J. Kim, D. S. Ellis, S. Wakimoto, R. J. Birgeneau, S. Komiyama, Y. Ando, B. Liang, R. L. Greene, D. Casa and T. Gog: Phys. Rev. Lett., 100 (9) (2008) 97001/1-4.

Fabrication of machinable AlN-BN composites with high thermal conductivity by pressureless sintering turbostatic BN-coated AlN nanocomposite powders, T. Kusunose, T. Sekino, Y. Ando and K. Niihara: J. Mater. Res., 23 (1) (2008) 236-244.

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Mechanical properties of  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$  polycrystals fabricated by the solid phase mixing and sintering method, H. Ohnishi, H. Naka, T. Sekino, Y. Ikuhara and K. Niihara: J. Ceram. Soc. Jpn., 116 (1351) (2008) 491-496.

Electrophoretic deposition behavior of ceria-stabilized zirconia/alumina powder, T. Nakamura, H. Nishida, T. Sekino, M. Nawa, K. Wakabayashi, S. Kinuta, Y. Mutoke and H. Yatani: Dent. Mater. J., 26 (5) (2007) 623-627.

Synthesis of photoresponsive azobenzene chromophore-modified multi-walled carbon nanotubes, Y. Y. Feng, W. Feng, H. Noda, T. Sekino, A. Fujii, M. Ozaki and K. Yoshino: Carbon, 45 (12) (2007) 2445-2448.

Production of a grain boundary phase as conducting pathway in insulating AlN ceramics, T. Kusunose, T. Sekino and K. Niihara: *Acta Mater.*, 55 (18) (2007) 6170-6175.

Contact damage of silicon carbide/boron nitride nanocomposites, T. Kusunose, T. Sekino and K. Niihara: *J. Am. Ceram. Soc.*, 90 (10) (2007) 3341-3344.

Preparation and characterization of chitosan-grafted multiwalled carbon nanotubes and their electrochemical properties, Z. G. Wu, W. Feng, Y. Y. Feng, Q. Liu, X. H. Xu, T. Sekino, A. Fujii and M. Ozaki: *Carbon*, 45 (6) (2007) 1212-1218.

Microstructure and crystal phase development of Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> polycrystal fabricated by the solid phase mixing and sintering method, H. Ohnishi, T. Fukuhara, T. Kawanami, T. Sekino, Y. Ikuhara and K. Niihara: *J. Ceram. Soc. Jpn.*, 115 (1339) (2007) 210-215.

The preparation and characterization of organic solvent dispersible polyaniline coated titania hybrid nanocomposites, Y. G. Han, T. Kusunose and T. Sekino: *Mater. Sci. Forum*, 569 (2008) 161-164.

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### **Review Papers**

Development of LaPO<sub>4</sub>-dispersed YSZ-based Ceramic Nanocomposite and Its Mechanical and Thermal Properties, T. Sekino, S. H. Kim, T. Kusunose: *The Journal of Fuel Cell Technology*, 7 [1], (2007) 85-92.

### **Books**

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### **Patents**

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### **International Conferences**

Transport Anisotropy as a Signature of Electron Nematicity (invited), \*Y. Ando: American Physical Society March Meeting (2008).

Transport Properties and Quantum Phase Transitions in Cuprates (invited), \*Y. Ando: International Workshop on Conductor-Insulator Quantum Phase Transitions (2008).

Why Cuprate Superconductors are So Difficult to Understand: Learning from Transport Properties (invited), \*Y. Ando: International Symposium on Lattice Effects in Cuprate High Temperature Superconductors (LEHTSC2007).

Implication of the Mott-Limit Violation in High-Tc Cuprates (invited), \*Y. Ando: 8th International Conference on Spectroscopies in Novel Superconductors (SNS2007).

Implication of the Mott-Limit Violation in High-Tc Cuprates (invited), \*Y. Ando: Conference on Dynamics in Complex Systems -- DELFS III (2007).

Doping n-type carriers to Y123 system by La substitution for Ba (poster), \*K. Segawa, Y. Ando: International Symposium on Lattice Effects in Cuprate High Temperature Superconductors (2007).

Metal-to-Insulator crossover in  $\text{YBa}_2\text{Cu}_3\text{O}_y$  at very low temperatures and high magnetic fields (invited), \*K. Segawa, X. F. Sun, Y. Ando: 20th International Symposium on Superconductivity (2007).

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Large Magnetoresistance of Spin Origin in Cuprates and Cobaltates (invited), \*Y. Ando: 11th Sanken, 6th Nanotechnology Center and 1st MSTEC International Symposium (2008).

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Universal values for the static and dynamic critical exponents in thin-film and bulk

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Search for proximity effect in the local pairing temperature of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ , \*C. Parker, A. Pushp, K. K. Gomes, A. Pasupathy, G. Gu, S. Ono, Y. Ando, A. Yazdani: American Physical Society March Meeting (2008).

Hall effect signature of Fermi surface reconstruction in high-Tc superconductors, \*F. F. Balakirev, J. B. Betts, A. Migliori, I. Tsukada, Y. Ando, G. S. Boebinger: American Physical Society March Meeting (2008).

Quantum spin excitations through the metal-to-insulator crossover in  $\text{YBa}_2\text{Cu}_3\text{O}_y$ , \*S. Li, Z. Yamani, H. J. Kang, K. Segawa, Y. Ando, X. Yao, H. A. Mook, P. Dai: American Physical Society March Meeting (2008).

Temperature evolution of local pairing & electron-boson coupling in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ , \*K. K. Gomes, A. Pasupathy, A. Pushp, C. Parker, G. Gu, S. Ono, Y. Ando, A. Yazdani: American Physical Society March Meeting (2008).

Electronic Origin of the Nanoscale Variation of Pairing Gaps in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ , \*A. Pasupathy, K. K. Gomes, A. Pushp, C. Parker, G. Gu, S. Ono, Y. Ando, A. Yazdani: American Physical Society March Meeting (2008).

Temperature Evolution of the Electronic States & Multiple Gap Features in  $\text{Bi}_2\text{Sr}_{2-y}\text{La}_y\text{CuO}_6$ , \*A. Pushp, A. Pasupathy, K. K. Gomes, C. Parker, S. Ono, Y. Ando, A. Yazdani: American Physical Society March Meeting (2008).

An infrared study of the pancake vortex state in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  across the phase diagram, \*A. Schafgans, A. Laforge, S. Dordevic, M. Qazilbash, S. Komiya, Y. Ando, D. Basov: American Physical Society March Meeting (2008).

Scanning Josephson Tunneling Microscopy of Single Crystal  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  from a Conventional Superconducting Tip, \*H. Kimura, R. Barber, S. Ono, Y. Ando, R. Dynes: American Physical Society March Meeting (2008).

Appearance of Universal Metallic Dispersion in a Doped Mott Insulator, \*H. Lin, S. Sahrakorpi, R. S. Markiewicz, X. J. Zhou, T. Yoshida, W. L. Yang, T. Kakeshita, H. Eisaki, S. Uchida, S. Komiya, Y. Ando, Z.X. Zhao, T. Sasagawa, A. Fujimori, Z. Hussain, Z. X. Shen, A. Bansil: American Physical Society March Meeting (2008).

Nitride Based Ceramic Nanocomposites with Multifunctionality (invited), \*T. Kusunose, T. Sekino, K. Niihara: The Sixteenth (2007) International Offshore and Polar Engineering Conference (ISOPE2007).

Non-Oxide Ceramic Nanocomposites with Multifunctionality (invited), \*T. Kusunose: 2nd International Symposium on SiAlONs and Non-oxides (2007).

Photocatalytic Properties of Titanium Oxide Nanotubes for Environmental and Energy Applications (invited), \*T. Sekino, A. Hayashi, T. Kusunose, S. Seino: International Joint Conference on Knowledge Management for Composite Materials: Symposium on Alternate Energy & Fuel Cell Technology (KMCM2007).

Development and Performance of Organic-Inorganic Nano-hybrid Pressure Sensor Materials (invited), \*T. Sekino, Y. G. Han, K. Kawahara, K. Murata, Y. Hamahashi, Y. Okamoto, H. Nishida, K. Niihara: The 2nd International Symposium on Organic and Inorganic Electronic Materials and Related Nanotechnologies (EM-NANO 2007).

Basics and Application of Ceramic and Polymer based Nanocomposite Materials (invited), \*T. Sekino: HFM Academic Forum 2007 -Educational Seminar on the Nanoscience and Nanotechnology for Advanced Materials-.

Synthesis and Properties of Oxide Ceramic Semiconductors with Thermoelectric Functions, \*T. Sekino, H. Hashimoto, Y. Saijo, T. Kusunose, T. Adachi, M. Sasaki: The Third International Workshop for R&D Clustering among China, Japan, Korea in Eco-Materials Processing (2007).

Characterization of 3YSZ/LaPO<sub>4</sub> Systems to Apply Thermal Barrier Coating, \*S. H. Kim, T. Kusunose, S. W. Lee, T. Sekino: The 7th Pacific Rim Conference on Ceramic and Glass Technology (PacRim7)(2007).

Multifunctionality of Titanium Oxide Nanotube and Its Nanocomposites, \*T. Sekino, A. Hayashi, D. J. Park, S. Itano, T. Nakayama, T. Kusunose, S. Seino: The 7th Pacific Rim Conference on Ceramic and Glass Technology (PacRim7)(2007).

Study of Conductive Elastomer Composites reinforced with Sulfonic Acid Doped Polyaniline Coated Titanium Dioxide (poster), \*Y. G. Han, T. Kusunose, T. Sekino: The 7th Pacific Rim Conference on Ceramic and Glass Technology (PacRim7)(2007).

Synthesis and Characterization of Various Shaped Au nanoparticles with Mixed Surfactant System (poster), \*S. Y. Moon, T. Kusunose, T. Sekino: The 7th Pacific Rim Conference on Ceramic and Glass Technology (PacRim7)(2007).

Design of 3D Nano-Network and Multi-Functions for Zirconia-Based Multi-Phase Nanocomposites Dispersed with CNT and Nanoparticles (invited), \*T. Sekino, X. P. Ye, S. H. Kim, T. Kusunose: The 9nd International Symposium on Eco-materials and Processing Design (ISEPD2008).

The Controlled Synthesis of Various Shape and Size of Gold Nanoparticles in Different Media, \*S. Y. Moon, T. Kusunose, T. Sekino: The 9nd International Symposium on Eco-materials and Processing Design (ISEPD2008).

h-BN Dispersed Silica Based Hybrid Coatings for Corrosion Protection, \*M. J. Cho, S. H. Kim, T. Kusunose, T. Nakayama, T. Sekino, K. Niihara: The 9nd International Symposium on Eco-materials and Processing Design (ISEPD2008).

The Preparation and Characterization of Organic Solvent Dispersible Polyaniline Coated Titania Hybrid Nanocomposites, \*Y. G. Han, T. Sekino, T. Kusunose: The 9nd International Symposium on Eco-materials and Processing Design (ISEPD2008).

Novel Adsorption and Photocatalytic Properties of Titania Nanotube in Liquid and Gas Phases (poster), \*A. Hayashi, D. J. Park, T. Kusunose, S. Seino, T. Sekino: The 9nd International Symposium on Eco-materials and Processing Design (ISEPD2008).

Development of P/n Oxide Semiconductor Composites Using Self-Organized Phase-Separation Control (poster), \*T. Shimizu, T. Kusunose, T. Sekino: The 9nd International Symposium on Eco-materials and Processing Design (ISEPD2008).

Thermoelectric Properties of Two Types Rare Earth Containing Cobalt Oxide Ceramics (poster), \*H. Hashimoto, T. Kusunose, T. Sekino: The 9nd International Symposium on Eco-materials and Processing Design (ISEPD2008).

#### **Contributions to International Conferences and Journals**

Y. Ando                      9th International Conference on Materials and Mechanisms of Superconductivity and High Temperature Superconductors (Organizing Committee)

#### **Publications in Domestic Meetings**

|                                               |           |
|-----------------------------------------------|-----------|
| Physical Society of Japan                     | 2 papers  |
| Ceramic Society of Japan                      | 10 papers |
| Japan Society of Powder and Powder Metallurgy | 3 papers  |

#### **Academic Degrees**

##### **Master Degree for Engineering**

|            |                                                                                                                     |
|------------|---------------------------------------------------------------------------------------------------------------------|
| T. Shimizu | Design and Evaluation of Spinodal-decomposed SnO <sub>2</sub> -TiO <sub>2</sub> System Doped with Metal Cations.    |
| A. Hayashi | Synergy of Adsorption and Photocatalytic Functions in Titanium Oxide Nanotubes.                                     |
| X. YE      | Development and Properties of Zirconia-based Multiphase Nanocomposites Dispersed with CNTs and Metal Nanoparticles. |

##### **Bachelor Degree for Engineering**

|          |                                                                                                                                        |
|----------|----------------------------------------------------------------------------------------------------------------------------------------|
| K. Etoh  | Synthesis of insulating PbS for the confirmation of spin-Hall effect                                                                   |
| T. Misao | Synthesis and characterization of Na <sub>x</sub> WO <sub>3</sub> for the investigation of possible high-temperature superconductivity |

#### **Sponsorship**

**Grant-in-Aid for Young Scientists (S)**

|         |                                                                                             |              |
|---------|---------------------------------------------------------------------------------------------|--------------|
| Y. Ando | Mott Insulator and Spin Hall Insulator:<br>Elucidating the Physics of Nontrivial Insulators | ¥ 17,940,000 |
|---------|---------------------------------------------------------------------------------------------|--------------|

**Grant-in-Aid for Scientific Research (B)**

|         |                                                                                              |             |
|---------|----------------------------------------------------------------------------------------------|-------------|
| Y. Ando | Electron Self-Organizations and Transport<br>Phenomena in High-Tc Cuprate<br>Superconductors | ¥ 4,582,163 |
|---------|----------------------------------------------------------------------------------------------|-------------|

**Grant-in-Aid for Scientific Research (B)**

|           |                                                                                                                            |            |
|-----------|----------------------------------------------------------------------------------------------------------------------------|------------|
| T. Sekino | Multiple Structuralization and Functionalization<br>of Oxide Nanotubes aiming for Environmental<br>and Energy Application. | ¥1,938,175 |
|-----------|----------------------------------------------------------------------------------------------------------------------------|------------|

**Grant-in-Aid for JSPS Fellows**

|             |                                                                                                                 |            |
|-------------|-----------------------------------------------------------------------------------------------------------------|------------|
| N. F. Fahim | Electrochemical Processing of Highly Oriented TiO <sub>2</sub><br>Nanotube Arrays for Solar Energy Applications | ¥1,200,000 |
|-------------|-----------------------------------------------------------------------------------------------------------------|------------|

**Entrusted Research**

|             |                             |                                                                 |            |
|-------------|-----------------------------|-----------------------------------------------------------------|------------|
| T. Kusunose | JST<br>Feasibility<br>Study | Synthesis of SiC/BN<br>Nanocomposite Powder for<br>Die and Mold | ¥1,000,000 |
|-------------|-----------------------------|-----------------------------------------------------------------|------------|

**Contribution to Research**

|             |                                     |            |
|-------------|-------------------------------------|------------|
| T. Sekino   | Otsuka Chemical Co., Ltd.           | ¥600,000   |
| T. Sekino   | Inaba Rubber Co., Ltd.              | ¥3,000,000 |
| T. Sekino   | Nippon Electric Glass Co., Ltd.     | ¥1,000,000 |
| T. Sekino   | Nikkato Corporation                 | ¥1,000,000 |
| T. Kusunose | Sumikin Ceramics & Quartz Co., Ltd. | ¥1,000,000 |
| T. Kusunose | Nippon Tungsten Co., Ltd.           | ¥500,000   |
| T. Kusunose | Tosoh Corporation                   | ¥1,350,000 |

**Cooperative Research**

|           |                                                                |                                                                                           |            |
|-----------|----------------------------------------------------------------|-------------------------------------------------------------------------------------------|------------|
| Y. Ando   | Central Research<br>Institute of<br>Electric Power<br>Industry | Development of new<br>materials by physically<br>understanding transition metal<br>oxides | ¥2,000,000 |
| T. Sekino | Tomoe Works Co.<br>Ltd.                                        | Development of Novel<br>Functional Nanocomposite<br>Coatings                              | ¥650,000   |

**Other Research Fund**

|           |                                                                      |                                                                                                           |          |
|-----------|----------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|----------|
| T. Sekino | NEDO (Industrial<br>Technology<br>Research Grant<br>Program in 2004) | Highly Functionalization of Oxide<br>Nanotubes and Its Application to<br>Environmentally-Friendly Systems | ¥845,000 |
|-----------|----------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|----------|

## Department of Advanced-Energy Material

|                      |                                      |
|----------------------|--------------------------------------|
| Professor:           | Katsumi TANIMURA                     |
| Associate Professor: | Shin'ichiro TANAKA                   |
| Research Assoc.      | Ei'ichi INAMI,                       |
| Graduate Students:   | Taku Ichibayashi,                    |
| Support Staff:       | Sachiyo NOZAWA,<br>Masanobu NUNOGAKI |

### Outlines

For fabricating highly functional nano-structured devices in future technology, it is essential to establish the ways to control structures and compositions of materials in atomic levels. In this department, we aim to establish the fundamentals for controlling the *modes of condensation and of atomic binding in epitaxial processes* via excitation-induced atomic reactions. For this purpose, we have carried out extensive experimental studies in the following three categories:

- 1) the primary processes of the structural transformation induced by electronic excitation in solids,
- 2) ultrafast carrier dynamics on semiconductor surfaces,
- 3) excitation-induced structural changes of semiconductor surfaces.

An important approach, characteristic of our research group, is to use the experimental method to probe *directly* the primary processes involved in the dynamics of photoinduced atomic reactions. Optical excitation generate first electronic excited states in solids or on surfaces, and the ultrafast relaxation processes of the excited species play crucial roles in inducing the structural changes. Optical probing techniques, like transient grating, reflection and/or absorption is certainly sensitive methods to detect changes in dielectric functions of systems studied. However, the results obtained by optical methods remain essentially indirect. In our case, we use time-resolved photoemission spectroscopy to study the carrier dynamics in fs-temporal domain to determine electron distribution functions as a function of time, which gives direct information of temporal evolution of electronic systems. Also, just recently, we have started to construct a new experimental apparatus to measure time-resolved electron diffraction with fs-temporal resolution. This allows us to determine directly the structural changes in crystals under optical excitation, thus providing a powerful tool to study excitation-induced atomic reactions in condensed matters.

As topics in the first category, we have studied the primary processes of the dynamics of the photoinduced phase transition in quasi-one dimensional organic crystals, and in two-dimensional graphite crystals. As topics of the second categories, we have studied carrier dynamics on Si surfaces by means of femtosecond two-photon photoemission spectroscopy. And as the third topic, we have studied laser- or low-energy electron induced structural changes of clean surfaces of Si and InP by means of not only the direct imaging of the surface atomic structure and its changes by STM, but also highly sensitive detection of Si atoms emitted from surfaces in the time scale of femtosecond. Also, femtosecond laser-induced phase transformation of graphite to a new phase of diamond is a very recent topic we have studied.



## Current Research Project

### 1. Excitation-Induced Instability on Semiconductor Surfaces

By using STM for revealing structural changes on surfaces at the atomic level, we have studied the laser-induced and tunneling-current-induced structural changes on semiconductor surfaces via electronic processes. For all surfaces studied, the electronic excitation results in surface structural changes associated with bond breaking of constituent atoms incorporated in the intrinsic surface structures. Based on the extensive experimental results and theoretical consideration, we have established a unified theoretical mechanism of the instability that can describe quantitatively the efficiency of surface bond breaking successfully. The mechanism is based on the two-hole localization of valence holes at an intrinsic surface site.

In this year, we have obtained two new and important results; one is tunneling-hole injection that triggers the local bond rupture of surface P atoms on InP(110)-(1x1), and the other is intrinsic surface optical transition that also trigger the surface Si atoms on Si(111)-(2x1). These results have substantiated further our conclusion that two-hole localization is the dominant mechanism of local bond rupture on semiconductor surfaces.

### 2. Ultra-fast surface carrier dynamics on semiconductor surfaces studied by femtosecond two-photon photoelectron spectroscopy

We have studied the carrier dynamics on Si surfaces by means of two-photon photoelectron spectroscopy in order to elucidate the dynamics of photogenerated surface carriers, which play crucial roles in several photoinduced reactions on solid surfaces. Use of femtosecond laser for pump and probe pulses has a strong advantage for resolving the carrier dynamics directly. In particular, the new system based on a tunable OPA laser for pump pulses of 100-fs temporal width has opened a new breakthrough for studying the dynamics extensively.

Based on extensive basic studies to identify several photoemission peaks, based on the precise theoretical results for Si, we have identified the peak from the conduction band minimum (CBM). By probing the CBM photoemission peaks, we revealed the ultrafast relaxation of hot electrons generated in the X valley of the conduction band of Si. The photogenerated electrons at higher points in the X valley relax down to the CBM within 100 fs, characterized by the intra-valley scattering time of 50 fs, and form the quasi-equilibrated electronic system characterized by the electron temperature  $T^*$ . Then, the cooling, or thermalization with lattice starts via electron phonon interaction with the energy relaxation time of 240 fs. These findings provide directly the hot-electron relaxation in Si, that was only speculated from previous optical studies.

By probing both the electrons in the bulk conduction band and those in surface-specific states of the Si(001)-(2x1) and Si(111)-(7x7) surfaces, we have found an ultrafast electron-hole recombination via surface localized state with 1 ps of excitation. Also, the lifetime of the surface  $D_{\text{down}}$  state is 15 ps, and has an effective surface electron-hole recombination, thus leading to strong density-dependent kinetics of carrier dynamics on this surface. At longer time delays, the transition from bulk-to-surface states is rate-determining of the surface-state population. Consequently, apparent decay of electrons at surface un-occupied state of  $D_{\text{down}}$  shows a strong excitation-wavelength

dependent feature.

### **3. Highly functional Surface-layer formation by Means of Charged-particle Irradiation and Plasma Processing**

We have developed a multiplex surface processing for creating “a new type metal ceramics” which have the properties of high thermal loading. The multiplex processing is the sequential process of the reactive modification of metal surfaces by irradiation with charged particle beams, followed by plasma processing for carburization, nitridation or oxidation. For establishing the method of this unique processing, we have constructing moving electrodes, which make it possible of ion-beam irradiation and plasma processing for the same samples without breaking high vacuum condition. The electrodes have given a reasonable performance in intensity and in stability.

In this year, we have succeeded to modify Ti into a thick TiC ceramic layers by using reactive plasma processing. The hardness have increased dramatically, and it reaches 5000 kg/mm<sup>2</sup> at a processing temperature of 1300 C. The mechanistic understanding of the abnormal hardness of TiC formed is now underway.

## **Publications**

### **Original Papers**

Fermi-level dependent morphology in photoinduced structural instability on (110) surfaces of III-V semiconductors, J. Kanasaki, E. Inami, and K. Tanimura, *Surf. Sci.* 601, 2367-2372 (2007).

Identification of the conduction-band photoemission in time-resolved two-photon photoemission spectroscopy of Si surfaces, T. Ichibayashi and K. Tanimura, *Phys. Rev. B* 75, 235327-1-6 (2007).

Electronic bond rupture of Si atoms on Si(111)-(2x1) induced by valence excitation, E. Inami and K. Tanimura, *Phys. Rev. B* 76, 035311-1-11 (2007).

Surface modification of a metal into a thick ceramic layer and a model for analyzing the increased hardness, S. Emura, M. Nunogaki, and Y. Nakata, *J. Ceram. Process. Res.* 8, 191-194 (2007).

Atomic structure analysis of Pd nanocluster in nanocomposite Pd/ZrO<sub>2</sub> absorbing Deuterium, S. Emura, Y. Arata, Y. Arachi, M. Nunogaki, and A. Ohmura, *高温学会誌*, 33, 142-156 (2007).

Scanning tunneling microscopy study on hydrogen removal from Si(001)-(2x1):H surface excited with low-energy electron beams, J. Kanasaki, K. Ichihashi, and K. Tanimura, *Surf. Sci.* 602, 1322-1327 (2008).

### **International Conferences**

Excitation-Induced Atomic Desorption and Structural Instability of Semiconductor



# Division of Organic Molecular Science

## Outline

Division of Organic Molecular Science has five departments: Dep. of Regulatory Bioorganic Chemistry, Dep. of Organic Fine Chemicals, Dep. of Organic Molecular Materials, Dep. of Molecular Excitation Chemistry, Dep. of Synthetic Organic Chemistry, and Dep. of Analytical Molecular Chemistry (started from April 2004). The research field in the division covers organic chemistry, bioorganic chemistry, organometallic chemistry, physical organic chemistry, material chemistry, physical chemistry, analytic chemistry, photochemistry, and reaction kinetics. In each department research on own original subject is going on and in some cases joint projects between several departments are carried out.

## Achievement

- Development of molecular glue for DNA
- Photoregulation of RNA-ligand interaction by photoresponsive peptide and its aptamer obtained by in vitro selection
- Detection of single nucleotide polymorphisms by allele specific PCR
- Development of molecules binding to DNA repeat sequence
- Derivatization of fusicoccane diterpenoids to have anti-cancer activity
- Reverse chemogenomics on intracellular signal transductions
- Design and synthesis of bivalent inhibitors targeting interior and exterior protein surfaces
- Development of p-type and n-type semiconductors for organic electronics
- Construction of molecular wires with switching and insulation-covering functions
- Beam-controlled chemistry of DNA
- Multi-laser multi-step photochemistry
- Photocatalytic reactions of  $\text{TiO}_2$
- Photochemical control of protein function
- Synthesis and application of isoxazoline/isoxazole hybrid-type asymmetric ligands
- Immobilization of multicomponent consisting asymmetric catalysts
- Functionalized nanoparticle as an asymmetric catalyst
- Development of spiro chiral ionic liquids

## Department of Regulatory Bioorganic Chemistry

Professor: Kazuhiko Nakatani  
Research Associate: Da-Yang Zhou, Masaki Hagihara, Chikara Dohno  
Post Doctoral Fellows: Hanping He  
Graduate Students: Gosuke Hayashi, Kyong-in Ryu, Shin-nosuke Uno, Shiori Umemoto, Tomohiro Doura, Changfeng Hong, Tsuyoshi Yamamoto  
Under Graduate Students: Shun Sakai  
Research Assistance: Akiko Seo, Masako Igarashi  
Supporting Staff: Miho Ohama

### Outlines

We have studied on “Chemical Biology” and “Nano-Technology” based on synthetic organic chemistry. For chemical biology, we focused our attention on 1) molecular design of mismatch binding ligands, and 2) in vitro selection of RNA aptamer binding specific nucleic acid structure. Because DNA is not only a genetic materials but also an important organic materials consisting of C, H, O, N, and P atoms with ability of spontaneously forming a double helix. To use DNA as precision organic materials in nano-technology, we have studied on the chemical properties of DNA and on the synthesis of chemically modified DNA.

### Current Research Project

#### Fluorescent Detection of Single Nucleotide Difference using Cytosine Bulge Hairpin Primers

The technique for promptly detecting the genetic mutation is expected as a basis technology that supports the personalized medicine. In this laboratory, we have proposed the technology for genetic mutation detection that uses a small molecule binding to the mismatch and the bulge structure in the duplex DNA. The practical technology must be handy, accurate, and cheap in cost. To meet this demand, we did not study the chemical modification of DNA, but used the molecule selectively binding to the cytosine bulge. Upon binding to cytosine bulge, the fluorescence wavelength shifted the long wavelength by 30 nm. By using this characteristic fluorescence, we have studied to develop the method detecting single nucleotide polymorphisms. A primer having a cytosine bulge site in a hairpin structure and SNP recognition site at the end of 3' was prepared for PCR. Using this primer and fluorescent molecules, allele specific PCR was monitored in order to do SNP typing. As a result of having performed PCR with a template, a big difference was observed for a change of the fluorescence in a difference of a single base at 3' end of primer and succeeded in recognizing a difference of single nucleotide polymorphisms.

#### Molecular Design of Ligand Selectively Binding to the Human Telomeric Repeat

## Overhang

The telomeric sequence d(TTAGGG)<sub>n</sub> located at the 3' end of human genomic DNA plays important roles in protecting chromosomal ends from fusion, rearrangement, and translocation. In cancer cells the enzyme telomerase is activated maintains the length of the telomere for achieving the immortality. Therefore, the ligands that bind to telomere and inhibit its elongation are expected to be potential anti-cancer drugs. The single-stranded region of the d(TTAGGG)<sub>n</sub> repeat is known to form G-quadruplex structures *in vitro*. We synthesized a novel ligand naphthyridine tetramer (NT) and evaluated its specific binding to the human telomeric repeat sequences. The results from enzymatic analyses together with spectroscopic measurements clearly showed that NT did not inhibit telomerase but interfere the telomere elongation by a formation of unique hairpin structure on the template. The novel mode of NT binding to the human telomere sequence would be useful for the design of molecules in a next generation.

## Development of photoswitchable molecular glue for DNA

DNA molecular glue is a small synthetic ligand that can adhere two single-stranded DNAs that do not spontaneously hybridize with each other. For reversible control of DNA hybridization by an external light stimulus, we have developed a photoswitchable molecular glue for DNA. The photoswitchable molecular glue, **NCDA**, consists of two guanine-recognizing naphthyridine moieties connected with a photochromic azobenzene unit. Azobenzene undergoes a reversible cis/trans isomerization by photoirradiation, which changes the relative orientations and positions of the naphthyridine moieties, resulting into photoswitching of **NCDA** binding to the DNA containing GG-mismatch. **NCDA** in the cis configuration binds to a GG-mismatch sequence, and induces the formation of the DNA duplex. Using the photoswitchable binding property of **NCDA**, the hybridization event of two natural unmodified DNAs can be reversibly controlled by an external light stimulus.

## Synthesized DNA bearing transition metal chain

Synthesis of DNA containing metal molecular chain is important in terms of production of novel materials. We have studied to synthesize a DNA which includes a transition metal molecular chain. We have synthesized a DNA bearing a copper-bipyridine group.

## Publications

### Original Papers

Detection of L-DNA-Tagged PCR Products by Surface Plasmon Resonance Imaging, Hayashi, G.; Hagihara, M.; Kobori, A.; Nakatani, K. ChemBioChem. 8 (2007) 169-171.

Bidirectional control of gold nanoparticle assembly by turning on and off DNA hybridization with thermally degradable molecular glue, Tao Peng, Chikara Dohno, Kazuhiko Nakatani, ChemBioChem, 8 (2007) 483-485.

Small-Molecule Binding to the Nonquadruplex Form of the Human Telomeric Sequence, Goto, Y.; Hagihara, S.; Hagihara, M.; Nakatani, K. ChemBioChem. 8 (2007) 723-726.

Allele Specific C-Bulge Probes with One Unique Fluorescent Molecule Discriminate the Single Nucleotide Polymorphism in DNA, Takei, F.; Suda, H.; Hagihara, M.; Zhang, J.; Kobori, A.; Nakatani, K. *Chem. Eur. J.* 13 (2007) 4452-4457.

Exploiting small molecule binding to DNA for the detection of single-nucleotide mismatches and their base environment, Xiaohong Li, Haifeng Song, Kazuhiko Nakatani, Heinz-Bernhard Kraatz, *Anal. Chem.* 79 (2007) 2552-2555.

The rare crystallographic structure of d(CGCGCG)(2): the natural spermidine molecule bound to the minor groove of left-handed Z-DNA d(CGCGCG)(2) at 10 degrees C., Hirofumi Ohishi, Yoshitaka Tozuka, Zhou Da-Yang, Toshimasa Ishida, Kazuhiko Nakatani, *Biochem. Biophys. Res. Commun.* 358 (2007) 24-28.

Analysis of mismatched DNA by mismatch binding ligand (MBL)-Sepharose affinity chromatography. Yuki Goto, Hitoshi Suda, Akio Kobori, Kazuhiko Nakatani, *Anal. Bioanal. Chem.* 388 (2007) 1165-1173.

Emission of characteristic fluorescence from the ligand-cytosine complex in U<sub>A</sub>/ACU bulged RNA duplex. Jinhua Zhang, Fumie Takei, Kazuhiko Nakatani, *Bioorg. Med. Chem.* 15 (2007) 4813-4817.

Stepwise functionalization of ribonucleopeptides: optimization of the response of fluorescent ribonucleopeptide sensors for ATP. Tetsuya Hasegawa, Masaki Hagihara, Masatora Fukuda, Takashi Morii, *Nucleosides, Nucleotides, & Nucleic Acids* 26 (2007) 1277-1281.

Photoregulation of a Peptide-RNA Interaction on a Gold Surface, Hayashi, G.; Hagihara, M.; Dohno, C.; Uno, S.; Nakatani, K. *J. Am. Chem. Soc.* 129 (2007) 8678-8679.

Photoswitchable Molecular Glue for DNA, Dohno, C.; Uno, S.; Nakatani, K. *J. Am. Chem. Soc.* 129 (2007) 11898-11899.

Polyamines stabilize left-handed Z-DNA: Using X-ray crystallographic analysis, we have found a new type of polyamine (PA) that stabilizes left-handed Z-DNA, Ohishi, H.; Odoko, M.; Grzeskowiak, K.; Hiyama, Y.; Tsukamoto, K.; Maezaki, N.; Ishida, T.; Tanaka, T.; Okabe, N.; Fukuyama, K.; Zhou, D.-Y.; Nakatani, K. *Biochem. Biophys. Res. Commun.* 366 (2008) 275-280.

The crystallographic study of left-handed Z-DNA d(CGCGCG)<sub>2</sub> and thermine complexes crystallized at various temperatures and at various concentration of cations, Ohishi, H.; Odoko, M.; Zhou, D.-Y.; Tozuka, Y.; Okabe, N.; Nakatani, K.; Ishida, T.; Grzeskowiak, K. *Biochem. Biophys. Res. Commun.* 368 (2008) 382-387.

Ligand-Stabilized Hairpin Structures Interfered with Elongation of Human Telomere Hagihara, Masaki; Goto, Yuki; Nakatani, Kazuhiko *ChemBioChem*, 9 (2008) 510-513.

### **International Conferences**

Mismatch-Binding Ligands as a Molecular Glue for DNA, \*Dohno, C., Peng, T., Nakatani, K., 7th International Meeting on Recognition Studies in Nucleic Acids, Sheffield, UK, Apr1-5, 2007

Photoswitchable Mismatch-Binding Ligands Control DNA Hybridization, Dohno, C., \*Uno, S., Oku, M., Nakatani, K., 7th International Meeting on Recognition Studies in Nucleic Acids, Sheffield, UK, Apr1-5, 2007

Mismatch-Binding Ligands: Chemistry Approach to Genotyping, International Symposium on Advanced Functional Genomics, \*Kazuhiko Nakatani, Kazusa DNA Research Institute, Chiba, Japan, October 11, 2007.

Molecular Glue for DNA, The 13th Korea-Japan Seminar on Organic Chemistry, \*Kazuhiko Nakatani, Department of Chemistry, KAIST, Daejeon (Korea), October 20-21, 2007.

Reversible regulation of binding between a photoresponsive peptide and its RNA aptamer, \*Hayashi, G., Hagihara, M., Dohno, C., Oku, M., Nakatani, K., 5th International Symposium on Nucleic Acids Chemistry, Tokyo, Japan, Nov20-22, 2007.

Reversible Control of DNA Hybridization by Photoresponsive Ligands, \*Uno, S., Dohno, C., Oku, M., Nakatani, K., 5th International Symposium on Nucleic Acids Chemistry, Tokyo, Japan, Nov20-22, 2007.

Application for the Fluorescent Detection of Single Nucleotide Difference using Cytosine Bulge Hairpin Primers, \*Fumie Takei, Masaki Hagihara, Yoshimi Oka, Kazuhiko Nakatani, 11th Sanken International Symposium, Awaji, Japan, Feb2-4, 2008.

Switching DNA hybridization by a molecular glue for DNA, \*Tsuyoshi Yamamoto, Chikara Dohno, Shin-nosuke Uno, Kazuhiko Nakatani, 11th Sanken International Symposium, Awaji, Japan, Feb2-4, 2008.

Displacement Assay For RNA-ligand Interactions, Using Ligand's Fluorescent Property, \*Shiori Umemoto, Jinhua Zang, Kazuhiko Nakatani, 11th Sanken International Symposium, Awaji, Japan, Feb2-4, 2008.

Molecular Glue for DNA, \*Chikara Dohno, NSF-MEXT US/Japan Young Scientists Symposium on Nanoscale Devices & Systems, Evanston, IL, USA, Mar-11, 2008.

### **Publications in Domestic Meetings**

Japan Chemical Society Meeting:  
Symposium on Nucleic Acids Chemistry

8 papers  
2 papers



|                                                |          |
|------------------------------------------------|----------|
| Sanken International Symposium                 | 4 papers |
| Japanese Society for Chemical Biology Meeting: | 3 paper  |
| Symposium on Biofunctional Chemistry           | 1 paper  |
| RNA Meeting 2007                               | 1 paper  |
| Symposium on Photochemistry                    | 1 paper  |
| SORST Joint Symposium                          | 2 paper  |

## Academic Degrees

### Master Degree for Science

K. Ryu

## Sponsorship

### Grant-in-Aid for Scientific Research (S)(C)

|             |                                                                                   |             |
|-------------|-----------------------------------------------------------------------------------|-------------|
| K. Nakatani | Regulation of DNA Structure and Function Based on the Stabilization of DNA Duplex | ¥34,500,000 |
| Z. Da-Yang  | Synthesis of Novel Cyclic Nucleotides Library by Metal-Catalyst                   | ¥2,340,000  |
| F. Takei    | Development of SNP detection method with modified PCR primers                     | ¥1,820,000  |

### Grant-in-Aid for Young Scientists (B)

|          |                                                          |            |
|----------|----------------------------------------------------------|------------|
| C. Dohno | Development of Photo-Responsive Mismatch Binding Ligands | ¥1,800,000 |
|----------|----------------------------------------------------------|------------|

### Entrusted Research

|             |                                     |                                                                                   |            |
|-------------|-------------------------------------|-----------------------------------------------------------------------------------|------------|
| K. Nakatani | Japan Science and Technology Agency | On-time detection of DNA higher order structure by the structure specific probes  | ¥5,900,000 |
| K. Nakatani | Japan Science and Technology Agency | SNP detection method by allele-specific PCR with allele specific C-bulge probes   | ¥4,100,000 |
| K. Nakatani | Japan Science and Technology Agency | Development of high throughput screening method for finding the RNA-binding drugs | ¥1,538,000 |

### Cooperative Research

|             |                      |                                                                                            |            |
|-------------|----------------------|--------------------------------------------------------------------------------------------|------------|
| K. Nakatani | KYOWA Hakko          | Establishment of methodology for molecular design of RNA-interacting small molecular drugs | ¥2,618,181 |
| K. Nakatani | NITTO Kasei co., ltd | Synthesis of DNA-binding molecule                                                          | ¥806,400   |

**Other Research Fund**

|             |                                 |              |                                                     |            |
|-------------|---------------------------------|--------------|-----------------------------------------------------|------------|
| M. Hagihara | Young<br>Investigators<br>Award | Year<br>2007 | The biological role of tandem<br>repeats in genomes | \$93,250   |
| K. Nakatani | The<br>Glass<br>Foundation      | Asahi        |                                                     | ¥5,000,000 |

**Awarded Degree**

Master (Science)

Keongim Yu

Synthesis and evaluation of a novel GG-mismatch binding ligand interacting with human telomere sequence

## Department of Organic Fine Chemicals

|                          |                                                                                                                                                                       |
|--------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Professor:               | Nobuo KATO                                                                                                                                                            |
| Associate Professor:     | Junko OHKANDA                                                                                                                                                         |
| Assistant Professor:     | Hajime NITTA                                                                                                                                                          |
| Appointed Researcher:    | Masamitsu HIRAOKA                                                                                                                                                     |
| Graduate Students:       | Takatsugu INOUE, Shinnosuke MACHIDA,<br>Yu HARANOSONO, Yusuke HIGUCHI, Toshio MAKI,<br>Shinya MIYAKE, Shinjiro SAWADA, Kohei FUJII,<br>Yuriko MARUYAMA, Takaaki MONTA |
| Under Graduate Students: | Chihiro KONDO                                                                                                                                                         |
| Supporting Staff:        | Misuzu TANNO                                                                                                                                                          |

### Outlines

The object of this department is to create lead compounds for drug discovery. Based on chemical proteomic approaches, our research interests are focused on the rational design and synthesis of small organic compounds that potentially modulate/inhibit protein-protein interactions. These compounds are also utilized as a tool in our chemical genomic study to elucidate intracellular signalling pathways. The protein surface-directed proteomimetic and peptidomimetic designs are also investigated. The stereoselective synthesis of biologically active compounds and the construction of biomimetic supramolecular systems are also investigated.

### Current Research Project

#### Identification of fusicoccane synthase

We found that (+)-fusicocca-2,10(14)-diene, a tricyclic hydrocarbon precursor for fusicoccins, is biosynthesized from the C<sub>5</sub> isoprene units by an unusual multifunctional enzyme identified in fusicoccin-producing fungus, *Phomopsis amygdali*. The enzyme (PaFS) shows both prenyltransferase and terpene cyclase activities. In fact, heterologous expression of PaFS alone resulted in the accumulation of fusicocca-2,10(14)-diene in *Escherichia coli* cells.

#### Synthesis of fusicoccin derivatives that have differentiation-inducing activity

We have already synthesized ISIR-005, a 12-deoxy derivative of fusicoccin, that induces functional and morphological differentiation of human myeloid leukemia cells (HL-60). ISIR-005 showed desirable biological activities as a new type of anti-cancer agent. However, its little solubility in water is troublesome for clinical trials. To overcome this problem, we have synthesized a number of fusicoccin derivatives. As a result, we could have ISIR-042, of which physicochemical properties are largely improved without loss of the activity. ISIR-042 is water soluble and gives crystalline salt with citric acid.

#### Bivalent geranylgeranyltransferase-I inhibitors for simultaneous targeting interior and exterior Protein surfaces

Modulation of protein-protein interactions by small organic agents still remains a difficult challenge due to the large interfacial areas of buried surface involved in such interactions. As an attempt to improve binding selectivity of the organic agents to targeting protein surface, a series of bivalent enzyme inhibitors consisting two distinct modules, which were designed for complementary recognition of characteristic protein interior and exterior surfaces of mammalian Type-I geranylgeranyltransferase, was synthesized. The bivalent compounds showed submicromolar inhibition activity against GGTase-I whereas each module compounds either showed lower potency or no activity. The detail kinetic studies of the inhibition of GGTase-I by the bivalent compound using fluorescent-tagged and radio labeled substrate clearly revealed that the inhibition mode is competitive, and that the selectivity for GGTase-I over FTase retains in more than 150 times, demonstrating that our anchoring strategy to target protein exterior surface does not compromise the selectivity.

#### **Chemical ligation of epoxide-containing fusicoccins and peptide fragments induced by 14-3-3 protein surface**

Dimeric 14-3-3 proteins are involved in regulation of phosphorylated Thr/Ser signaling pathways. Each monomer possesses a highly conserved amphipathic cleft that binds to a consensus motif containing phosphorylated Thr or Ser. A fungus phytotoxin fusicoccin (FC) has been found to bind to a hydrophobic site in the cleft and stabilizes the complex of 14-3-3 bound to a peptide QSYpTV by 90-fold. We designed and synthesized the ligation modules based on FC and QSYpTV, which were chemically modified by introducing an epoxide and a thiol group at appropriate position by a spacer, respectively. The HPLC analysis of the epoxide ring opening reaction in presence or in absence of 14-3-3 in Tris buffer (pH 9.0) at 25 °C showed that the reaction efficiency was enhanced up to 200% when the equimolar amount of 14-3-3 was added.

#### **New synthetic method of 4-carbamoyl-5-hydroxyimidazole**

4-Carbamoyl-5-hydroxyimidazole (SM-108) has potent anti-tumor activities, especially, has the excellent medicinal properties for myelodysplastic syndromes (MDS). In fact, Phase II clinical trial had been conducted and the results were quite promising. However, further clinical development of SM-108 discontinued because of its instability and the colorants formation during its synthetic process. We have modified the synthetic procedures and, eventually, established the new synthetic method, with which pure and stable benzenesulfonic acid salt of SM-108 can be obtained easily.

## **Publications**

### **Original Papers**

Farnesyltransferase and geranylgeranyltransferase I inhibitors upregulate RhoB expression by HDAC1 dissociation, HAT association and histone acetylation of the RhoB promoter, F. L. Delarue, J. Adnane, B. Joshi, M. A. Blaskovich, D. Wang, J. H. F. Bizouarn, J. Ohkanda, K. Zhu, A. D. Hamilton, S. Chellappan, and S. M. Sebti, *Oncogene*. 26 (2007) 633-640.

Fusicoccins are biosynthesized by an unusual chimera diterpene synthase in fungi, T. Toyomasu, M. Tsukahara, A. Kaneko, R. Niida, W. Mitsunashi, T. Daiiri, N. Kato, and T.

Sassa, Proc. Nat. Acad. Sci. USA. 104 (2007) 3084-3088.

Module assembly for protein-surface recognition: Geranylgeranyltransferase I bivalent inhibitors for simultaneous targeting of interior and exterior protein surfaces, S. Machida, K. Usuba, M. A. Blaskovich, A. Yano, K. Harada, S. M. Sebti, N. Kato, and J. Ohkanda, Chem. Eur. J. 14 (2008) 1392-1401.

### **Review Papers**

Synthetic inhibitors targeting protein surfaces (Perspective), J. Ohkanda, SAR News, The Division of Structure-Activity Studies, The Pharmaceutical Society of Japan, 13 (2007) 2-7.

Rational design and functional evaluation of antitumor activity of peptidomimetic prenyltransferase inhibitors, J. Ohkanda, News Letter of Division of Biofunctional Chemistry, The Chemical Society of Japan, 21 (2007) 25-28.

### **Patents**

Derivatives of 4-carbamoyl-5-hydroxyimidazole and their salts with several sulfonic acids, N. Kato, Y. Higuchi, C. Kondo, and M. Sunagawa, JP2007-238653 & JP2008-028268.

Fusicoccane Synthase and Its Gene, T. Toyomasu, T. Sassa, T. Daiiri, and N. Kato, PCT/JP2007/069337.

Membrane fusion inhibitors, K. Kaihatsu, S. Mori, T. Daidoji, S. Miyake, and N. Kato, JP2008-023196.

### **International Conferences**

Design and Evaluation of Bivalent Enzyme Inhibitors for Simultaneous Recognition of Interior and Exterior Protein Surfaces, \*J. Ohkanda, S. Machida, and N. Kato, Gordon Research Conference, Bioorganic Chemistry, New Hampshire, USA, June 10-15, 2007.

An Unusual Chimera Diterpene Synthase Is Responsible for Fusicoccin Biosynthesis, \*T. Toyomasu, M. Tsukahara, A. Kaneko, R. Niida, C. Ikeda, W. Mitsuhashi, T. Daiiri, N. Kato, and T. Sassa, 19th International Conference on Plant Growth Substances, Rivera Maya, Cancun, Mexico, July 21-25, 2007.

Bivalent Inhibitors of Type-I Geranylgeranyltransferase for Simultaneous Recognition of Interior and Exterior Protein Surfaces, \*J. Ohkanda, S. Machida, N. Kato, M. A. Blaskovich, S. M. Sebti, and K. Harada, American Chemical Society 234th National Meeting, Boston, USA, August 19-23, 2007.

Fusicoccin Derivatives as Therapeutic Agents Based on Induction of Differentiation, \*Y. Honma, M. Akimoto, T. Sassa, and N. Kato, 19th EORTC-NCI-AACR Symposium on "Molecular Targets and Cancer Therapeutics", San Francisco, USA, October 22-26, 2007.

Synthesis and Evaluation of VIS-Sensitive Azobenzene Derivatives for Controlling Cellular Gene Expressions, \*K. Kaihatsu, S. Sawada, and N. Kato, 11th Sanken International Symposium, Awaji, Japan, February 4-5, 2008.

Synthesis of Green Tea Catechin Derivatives and Evaluation of Their Anti-influenza Virus Activity, \*S. Mori, S. Miyake, K. Kaihatsu, and N. Kato, 11th Sanken International Symposium, Awaji, Japan, February 4-5, 2008.

Dual Inhibitors of Protein Prenyltransferase: Activity-tuning by Target Protein Surfaces, \*S. Machida, N. Kato, and J. Ohkanda, 11th Sanken International Symposium, Awaji, Japan, February 4-5, 2008.

Synthesis and Biological Evaluation of Fusicoccin Derivatives, \*T. Inoue, Y. Maruyama, H. Nitta, J. Ohkanda, and N. Kato, 11th Sanken International Symposium, Awaji, Japan, February 4-5, 2008.

### **Contributions to International Conferences and Journals**

|         |                                                                          |
|---------|--------------------------------------------------------------------------|
| N. Kato | 24th Conference on Combinatorial Chemistry, Japan (Conference Director)  |
| N. Kato | 25th Conference on Combinatorial Chemistry, Japan (Organizing Committee) |

### **Publications in Domestic Meetings**

|                                                                |          |
|----------------------------------------------------------------|----------|
| Japan Chemical Society Meeting                                 | 6 papers |
| Japan Society for Bioscience, Biotechnology, and Agrochemistry | 3 papers |
| Meeting of West Japan Branches of CSJ                          | 2 papers |
| The Pharmaceutical Society of Japan                            | 1 paper  |
| The Japanese Cancer Association                                | 1 paper  |
| Chem-Bio Informatics Society                                   | 1 paper  |
| Informal Symposium on Organic Reactions                        | 1 paper  |
| Forum on Biomolecular Chemistry                                | 1 paper  |
| Symposium on the Chemistry of Biocatalysis                     | 1 paper  |
| Japanese Society for Biomaterials                              | 1 paper  |

### **Academic Degrees**

#### **Doctor Degree for Science**

|            |                                                                                                                     |
|------------|---------------------------------------------------------------------------------------------------------------------|
| M. Hiraoka | Design and Synthesis of Inhibitors Targeting Autoinducer-2-dependent Quorum Sensing System in <i>Vibrio harveyi</i> |
|------------|---------------------------------------------------------------------------------------------------------------------|

#### **Master Degree for Science**

|               |                                                                              |
|---------------|------------------------------------------------------------------------------|
| Y. Haranosono | Synthetic studies on inhibitors of metallo- $\beta$ -lactamases              |
| Y. Higuchi    | Synthetic modification of fusicoccin aglycone to have anti-cancer activities |

|           |                                                                           |  |
|-----------|---------------------------------------------------------------------------|--|
| T. Maki   | Study on module assembly targeting 14-3-3 protein surface                 |  |
| S. Miyake | Synthesis and anti-influenza evaluation of novel tea catechin derivatives |  |

## Sponsorship

### Grant-in-Aid for Scientific Research on Priority Areas

|         |                                                                                                    |            |
|---------|----------------------------------------------------------------------------------------------------|------------|
| N. Kato | Analysis and Control of Intracellular Signal Transductions by Use of Diterpene Glycosides as Tools | ¥2,800,000 |
|---------|----------------------------------------------------------------------------------------------------|------------|

### Grant-in-Aid for Scientific Research (C)

|            |                                                                       |            |
|------------|-----------------------------------------------------------------------|------------|
| J. Ohkanda | Molecular Glue-Driven Module Assembly for Protein Surface Recognition | ¥1,000,000 |
|------------|-----------------------------------------------------------------------|------------|

### Grant-in-Aid for JSPS Fellows

|          |                                                      |          |
|----------|------------------------------------------------------|----------|
| T. Inoue | Forward and Reverse Chemogenomics on 14-3-3 Proteins | ¥900,000 |
|----------|------------------------------------------------------|----------|

### Entrusted Research

|         |                                                                                                                                                                         |             |
|---------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| N. Kato | Program for Development of new Promotion of anti-cancer agents based on Fundamental the differentiation-inducing Studies in diterpene glycoside Health Sciences (NIBIO) | ¥34,000,000 |
|---------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|

### Other Research Fund

|            |                             |                                                                                              |            |
|------------|-----------------------------|----------------------------------------------------------------------------------------------|------------|
| J. Ohkanda | Takeda Science Foundation   | Dual inhibitors of protein prenyltransferases: Activity-tuning by targeting protein surfaces | ¥2,000,000 |
| J. Ohkanda | Suzuken Memorial Foundation | Molecular Glue-driven in Vivo Module Assembly and Regulation of Protein Surface Function     | ¥1,000,000 |



## Department of Organic Molecular Materials

Professor: Yoshio ASO  
Research Associate: Yutaka IE  
Graduate Students: Yoshikazu UMEMOTO, Masaru ENDO,  
Masashi NITANI, Tomoya HIROSE,  
Toshihiko UTO, Makoto OKABE  
Under Graduate Students: Takahiro NOZAWA  
Supporting Staff: Misayo IMAI

### Outlines

The main subject in the Department of Organic Molecular Materials is the development of novel molecular-based materials with promising electronic and photoelectric properties for organic electronics. The research is based on the elucidation of the relationship between molecular structures and physical properties to control and improve the functions. We have been focusing our research on the design, synthesis, and properties of (1) novel extended conjugation systems as active materials for organic electronic and photoelectric devices and (2) nano-scale conjugated molecules for promising functional molecular wires. These nano-scale molecular materials have potential use as a fundamental framework for organic electronic devices.

### Current Research Project

#### Organic Electronics Materials

We have developed organic materials for n-type field-effect transistors. It has been known that the introduction of perfluoroalkyl groups into pi-conjugated systems dramatically increases their n-type character. We have designed hexafluorocyclopenta[*c*]thiophene, difluoromethylene-bridged bithiophene, bis(difluoromethylene)-bridged terphenylene, difluorodioxacyclopenta[*c*]thiophene, and difluorodioxacyclopenta[*b*]thiophene monomer units and synthesized their based conjugated oligomers. Their electronic absorptions, X-ray analyses, and redox potentials indicated that ring fusion of the fluoroalkylene units to aromatics not only keeps the planarity between consecutive aromatic rings but also increases n-type character. Some of these electronegative oligomers revealed high field-effect electron mobility, and hexafluorocyclopenta[*c*]thiophene homo-oligomer and the oligomers containing the difluoromethylene-bridged bithiophene unit or the difluorodioxacyclopenta[*b*]thiophene terminal unit showed the highest class of electron mobility.

In anticipation of self-association properties, we have synthesized the highly branched oligothiophenes with the juncture of 1,3,5-trisubstituted benzene for the development of high carrier-mobility materials in a film. The association constants revealed increasing association properties with increasing the number of branch points as well as the length of the central oligothiophenes. The FETs fabricated by spin coating from a solution of the branched oligothiophenes showed reasonably good p-type characteristics. Moreover, the branched-oligothiophene/[60]fullerene linkage molecules have been

synthesized, and their electronic properties were characterized by spectroscopic and electrochemical measurements. The FET devices were fabricated with their spin-coated films, and the appearance of ambipolar character indicates that the self-aggregation of the dendritic oligothiophene parts effectively contributes the formation of hole- as well as electron-transporting channels. The branched-oligothiophene/perylenebisimide linkage molecule has been also synthesized, and it showed good photovoltaic properties owing to highly efficient photo-induced intra- and intermolecular electron transfer.

### **Molecular Electronics Materials**

We have been preparing molecular wires for building up nanoelectronic devices with the use of the thiophene 24-mer with ca. 10 nm in length having insulating coverage around the oligomer chain. The cyclopentathiophene monomer units with bulky t-butyl-diphenylsilyl (TBDPS) groups or with a spiro-type substituted dioctylfluorene have been designed, and then a series of their oligomers up to 12-mer were synthesized. The electronic absorption maxima of the oligomers were found to be bathochromically shifted with increasing the number of thiophene rings, clearly indicating that the bulky groups have little influence on the effective conjugation. The X-ray analyses also revealed that the oligomeric backbone is completely insulated by the bulky groups. The electronic absorption spectra of oxidized species of these insulated oligothiophenes showed complete blocking of pi-dimer formations unlike usual oligothiophenes.

Moreover, it is highly important to connect each molecular wire to the bulk nano-gap electrode. We have achieved the synthesis of the thiophene 24-mers with terminal thiol anchor groups for gold electrodes as well as with terminal ethynyl anchor groups for silicon electrodes and succeeded in conduction measurement of the thiol-anchor molecular wire by use of a nano-gap gold electrode.

For certain connection of molecular wires with metal electrodes and efficient carrier injection, we have developed tetraphenylmethane tripodal anchor units with various functional groups and found unique adsorption properties of the selenium anchors on a gold electrode.

### **Publications**

#### **Original Papers**

Synthesis, Structures, and Spectroscopic Properties of Push-Pull Heteroquinoid Compounds, S. Inoue, S. Mikami, K. Takimiya, T. Otsubo: *Heterocycles*, 71 (2) (2007) 253-268.

Electrical Conductance Measurement of Oligothiophene Molecular Wires Using Nano-gap Electrodes Prepared by Electrochemical Plating, N. Hatanaka, M. Endo, S. Okumura, Y. Ie, R. Yamada, Y. Aso, K. Tanaka, H. Tada: *Chem. Lett.*, 36 (2) (2007) 224-225.

Synthesis of Dendritic Oligothiophenes and Their Self-Association Properties by Intermolecular pi-pi Interactions, N. Negishi, Y. Ie, M. Taniguchi, T. Kawai, H. Tada, T. Kaneda, Y. Aso: *Org. Lett.*, 9 (5) (2007) 829-832.

Synthesis of 10-nm Scale Oligothiophene Molecular Wires Bearing Anchor Units at

Both Terminal Positions, M. Endou, Y. Ie, T. Kaneda, Y. Aso: *J. Org. Chem.*, 72 (7) (2007) 2659-2661.

Bias Dependence of Tunneling-Electron-Induced Molecular Fluorescence from Porphyrin Films on Noble-Metal Substrates, H. W. Liu, Y. Ie, R. Nishitani, Y. Aso, H. Iwasaki: *Phys. Rev. B*, 75 (11) (2007) 115429-1-5.

Ambipolar Characteristics of Dendritic Oligothiophene/Fullerene Linkage Molecules, N. Negishi, Y. Ie, H. Tada, T. Kaneda, Y. Aso: *Chem. Lett.*, 36 (4) (2007) 544-545.

Electronegative Oligothiophenes for n-Type Semiconductors: Difluoromethylene-Bridged Bithiophene and Its Oligomers, Y. Ie, M. Nitani, M. Ishikawa, K.-i. Nakayama, H. Tada, T. Kaneda, Y. Aso: *Org. Lett.*, 9 (11) (2007) 2115-2118.

Polaron Dynamics in two Types of Long Oligothiophenes Revealed by Q- and X-Band ESR Measurements, K. Kanemoto, K. Furukawa, N. Negishi, Y. Aso, T. Otsubo: *Phys. Rev. B*, 76 (15) (2007) 155205-1-8.

Synthesis, Properties, and Structures of Difluoromethylene-bridged Coplanar p-Terphenyl and Its Aryl-capped Derivatives for Electron-transporting Materials, Y. Ie, M. Nitani, Y. Aso: *Chem. Lett.*, 36 (11) (2007) 1326-1327.

Substrate Effect of STM-Induced Luminescence from Porphyrin Molecules, H. W. Liu, Y. Ie, R. Nishitani, T. Z. Han, Y. Aso, H. Iwasaki: *Thin Solid Films*, 516 (9) (2008) 2727-2730.

Electronegative Oligothiophenes Based on Difluorodioxocyclopentene-Annelated Thiophenes: Synthesis, Properties, and n-Type FET Performances, Y. Ie, Y. Umemoto, M. Okabe, T. Kusunoki, K.-i. Nakayama, Y.-J. Pu, J. Kido, H. Tada, Y. Aso: *Org. Lett.*, 10 (5) (2008) 833-836.

Electronegative Oligothiophenes Fully Annelated with Hexafluorocyclopentene: Synthesis, Properties, and Intrinsic Electron Mobility, Y. Umemoto, Y. Ie, A. Saeki, S. Seki, S. Tagawa, Y. Aso: *Org. Lett.*, 10 (6) (2008) 1095-1098.

Perfluoroalkyl-Annelated Conjugated Systems towards n-Type Organic Semiconductors, Y. Ie, Y. Umemoto, M. Nitani, Y. Aso: *Pure Appl. Chem.*, 80 (3) (2008) 589-597.

## Books

Development, Electronic Functions, and Device Applications of Oligothiophene/Fullerene Hybrids (part), Y. Aso and Y. Ie, in *Handbook of Nano Carbon*, Ed. M. Endo and S. Iijima, NTS (2007) 639-644.

Synthesis and Functions of Oligothiophenes (part), Y. Aso and Y. Ie, in *Invention of Conjugated Electronic Structures: Synthesis, Functions, and Applications*, Ed. T. Hiyama, CMC (2008) 198-208.

## Patents

Conjugated Compounds and Their Organic Thin Films and Organic Thin-Film Devices, Y. Ie, Y. Aso, M. Okabe, and M. Ueda, JP2007-311381.

Compounds Consisting of Nitrogen-containing Condensation Ring, Polymers Consisting of Nitrogen-containing Condensation Ring, and Organic Thin Films and Organic Thin-Film Devices, Y. Ie, M. Nitani, Y. Aso, and M. Ueda, JP2008-031972.

Branched Compounds and Their Organic Thin Films and Organic Thin-Film Devices, Y. Ie, T. Uto, Y. Aso, and M. Ueda, JP2008-031973.

Polymers and Their Organic Thin Films and Organic Thin-Film Devices, M. Karakawa, Y. Aso, and M. Ueda, JP2008-032021.

## International Conferences

Fluoroalkyl-Annulated Conjugated Oligomers as n-Type Organic Semiconductors (invited), \*Y. Aso and Y. Ie: 12th International Symposium on Novel Aromatic Compounds, Awaji, Japan, July 22-27, 2007.

Thieno[3,2-d]imidazolium-containing Molecular Wire: Switching Behavior of Photoinduced Intramolecular Electron Transfer (poster), \*Y. Ie, T. Kawabata, T. Kaneda, and Y. Aso: 12th International Symposium on Novel Aromatic Compounds, Awaji, Japan, July 22-27, 2007.

Synthesis of 10-nm Scale Oligothiophene Molecular Wires Bearing Anchor Units at both Terminal Positions (poster), \*M. Endou, Y. Ie, T. Kaneda, and Y. Aso: 12th International Symposium on Novel Aromatic Compounds, Awaji, Japan, July 22-27, 2007.

Synthesis and Properties of Conjugated Oligomers Containing Perfluoroalkyl-bridged Terphenyl (poster), \*M. Nitani, Y. Ie, and Y. Aso: 12th International Symposium on Novel Aromatic Compounds, Awaji, Japan, July 22-27, 2007.

Synthesis and Properties of Cyclic Conjugated Oligomers having Benzothiophenes for Linkage Unit (poster), \*T. Hirose, Y. Ie, T. Kaneda, and Y. Aso: 12th International Symposium on Novel Aromatic Compounds, Awaji, Japan, July 22-27, 2007.

Synthesis and Electronics Application of Modified Oligothiophenes (invited), Y. Aso: Post-Symposium of ISNA in Himeji/Harima on Functional Aromatic Compounds, Hyogo, Japan, July 30-31, 2007.

Synthesis and Properties of Conjugated Oligomers Containing Perfluoroalkyl-bridged Terphenyl (poster), \*M. Nitani, Y. Ie, and Y. Aso: 11th SANKEN International Symposium 6th Nanotechnology Center International Symposium 1st MSTEC International Symposium – New Advances in Nanoscience & Nanotechnology -, Awaji, Japan, February 4-5, 2008.

Synthesis and Properties of Cyclic Oligothiophenes having Benzothiophenes for Linkage Unit (poster), \*T. Hirose, Y. Ie, and Y. Aso: 11th SANKEN International Symposium 6th Nanotechnology Center International Symposium 1st MSTEC International Symposium – New Advances in Nanoscience & Nanotechnology -, Awaji, Japan, February 4-5, 2008.

Synthesis of 10-nm Scale Oligothiophene Molecular Wires Bearing Anchor Units at both Terminal Positions (poster), \*M. Endou, Y. Ie, T. Kaneda, and Y. Aso: 11th SANKEN International Symposium 6th Nanotechnology Center International Symposium 1st MSTEC International Symposium – New Advances in Nanoscience & Nanotechnology -, Awaji, Japan, February 4-5, 2008.

Electronegative Oligothiophenes Based on Difluorodioxocyclopentene-Annelated Thiophenes: Synthesis, Properties, and n-Type FET Performances (poster), \*Y. Ie, M. Okabe, Y. Umemoto, and Y. Aso: 11th SANKEN International Symposium 6th Nanotechnology Center International Symposium 1st MSTEC International Symposium – New Advances in Nanoscience & Nanotechnology -, Awaji, Japan, February 4-5, 2008.

### **Contributions to International Conferences and Journals**

Y. Aso                                      12th International Symposium on Novel Aromatic Compounds  
(Organizing Committee, Financial Chair)

### **Publications in Domestic Meetings**

|                                            |          |
|--------------------------------------------|----------|
| The Chemical Society of Japan              | 4 papers |
| Symposium on Main Element Chemistry        | 1 paper  |
| Symposium on Organic pi-Systems            | 2 papers |
| Symposium on Structural Organic Chemistry  | 3 papers |
| The Chemical Society of Japan/Kanto Branch | 1 paper  |
| The Society of Polymer Science, Japan      | 1 paper  |

### **Academic Degrees**

#### **Doctor Degree for Engineering**

Y. Umemoto                              Development of Electronegative Oligothiophenes Based on  
Novel Fluorinated Cyclopentathiophenes

#### **Master Degree for Engineering**

M. Nitani                              Synthesis, Properties, and Field-Effect Characteristics of  
pi-Conjugated Oligomers Bridged with Electron-withdrawing  
Groups

T. Hirose                              Synthesis of Tripodal Anchor Units towards Control on the  
Electronic Nature and Characterization of Their Monolayers

### **Sponsorship**

**Grant-in-Aid for Scientific Research on Priority Areas**

|        |                                                                                                                      |            |
|--------|----------------------------------------------------------------------------------------------------------------------|------------|
| Y. Aso | Carrier-Transport Materials Based on<br>Extended-Conjugation Systems and Their Novel<br>Functions                    | ¥1,800,000 |
| Y. Aso | Development of Extended Conjugated Oligomers<br>toward Construction of Charge-Transporting<br>Hierarchical Structure | ¥1,500,000 |
| Y. Ie  | Development of Insulated Oligothiophene Molecular<br>Wires Bearing Tripodal Anchor Units at Terminal<br>Position     | ¥2,300,000 |

**Grant-in-Aid for Scientific Research for Young Scientists (B)**

|       |                                                                                        |            |
|-------|----------------------------------------------------------------------------------------|------------|
| Y. Ie | Development of Perfluoroalkyl-Bridged<br>Oligothiophenes Towards n-Type Semiconductors | ¥1,600,000 |
|-------|----------------------------------------------------------------------------------------|------------|

**Entrusted Research**

|        |                                        |                                           |            |
|--------|----------------------------------------|-------------------------------------------|------------|
| Y. Aso | Japan Science and Technology<br>Agency | Synthesis of Insulated Molecular<br>Wires | ¥5,070,000 |
|--------|----------------------------------------|-------------------------------------------|------------|

**Cooperative Research**

|        |                       |                              |            |
|--------|-----------------------|------------------------------|------------|
| Y. Aso | Sumitomo              | Development of Materials for | ¥4,070,000 |
| Y. Ie  | Chemical Co.,<br>Ltd. | Organic Electronics          |            |
| Y. Aso | Daikin                | Development of Ultra-low     | ¥1,000,000 |
| Y. Ie  | Industries, Ltd       | Reflection Materials         |            |

**Other Research Fund**

|       |                                                   |                                                                                                                        |            |
|-------|---------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|------------|
| Y. Ie | Foundation<br>Advanced<br>Technology<br>Institute | Development of<br>electron-transporting organic<br>semiconductor materials<br>based on innovative<br>molecular design. | ¥1,400,000 |
|-------|---------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|------------|

## Department of Molecular Excitation Chemistry

Professor: Tetsuro MAJIMA  
Associate Professor: Mamoru FUJITSUKA  
Research Associate: Sachiko TOJO, Takashi TACHIKAWA  
Visiting Professors: Akira SUGIMOTO  
Post Doctoral Fellows: Tadao TAKADA, Kohji NAKAYAMA,  
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Yoshiki MIYAMOTO, Man Jae PARK, Jun Rye CHOI,  
Ken HARADA, Hiromi URASAKI, Chunyan RIM,  
Shi-Cong CUI, Yuichiro TAKEDA, Takeshi NAKATANI,  
Under Graduate Students: Haruka KODERA  
Supporting Staff: Sanae TOMINAGA

### Outlines

"Beam-induced molecular chemistry" based on photo- and radiation-induced chemistry of organic compounds has been investigated from both basic and beam-functional points of view. The research topics are underway with respect to developments of new beam-controlled chemistry, new synthetic chemistry, and new molecular devices and functional materials.

1. Formation and reactivities of reactive intermediates in photochemistry and radiation chemistry, and photochemistry of reactive intermediates
2. Multi-beam chemistry with irradiation by two-color laser-laser and electron pulse-laser flash
3. Multiple-photon chemistry of organic compounds using UV, visible, and infrared lasers
4. Beam-controlled chemistry of artificial biomolecules such as modified DNA and proteins

### Current Research Project

#### Multi-beam Chemistry

Multi-beam chemistry has been studied using pulse radiolysis-laser flash photolysis combined method, two-color two-laser photolysis and three-color three-laser photolysis. Photochemistry of reaction intermediates and short-lived chemical species generated from the reaction induced by the first beam excitation of a starting molecule (two-step excitation method), and moreover, photochemistry of other chemical species generated from the reaction of the short-lived intermediate induced by the second beam excitation (three-step excitation method) can be studied. This year, by using the multi-beam irradiation method, we have determined the energy levels of the higher triplet excited states of oligothiophenes. Furthermore, we have demonstrated that energy transfer in the triad molecule of oligothiophene and energy acceptors can be controlled by the multi-laser irradiation. Furthermore, we have investigated hole transfer process of the

excited radicals and charge separation of the S<sub>2</sub>-excited porphyrins derivatives. In addition, we have clarified energy migration processes in alternating block copolymers of oligothiophene and oligosilylene and its model compounds. Excimer formation and charge separation in the dyad molecules of naphthaldiimide and phenothiazines are also clarified.

### **Mechanisms of TiO<sub>2</sub> Photocatalytic Reactions**

The single-molecule detection of airborne reactive oxygen species (ROS), such as singlet oxygen and hydroxyl radical, diffused from the photoirradiated TiO<sub>2</sub> (pure or nitrogen (N)-doped) surface, was successfully demonstrated using single-molecule fluorescence spectroscopy. Airborne single singlet oxygen molecules and hydroxyl radicals were selectively detected by the fluorescent probes, terrylenediimide and fluorescein derivatives, respectively. Upon UV excitation, both ROS were detected from both the pure and N-doped TiO<sub>2</sub> samples, while singlet oxygen was exclusively detected only from the N-doped TiO<sub>2</sub> upon visible excitation. Furthermore, the spatial and temporal distribution of the airborne hydroxyl radicals diffused from the photoirradiated TiO<sub>2</sub> surface was investigated by the real-time single-molecule imaging technique.

### **Charge Separation in DNA**

The formation of the long-lived charge-separated state in DNA upon visible light irradiation is of particular interest in molecular-scale optoelectronics, sensor design, and other areas of nano-technology. In this study, a series of protonated 9-alkylamino-6-chloro-2-methoxyacridine (Acr<sup>+</sup>) and phenothiazine (Ptz) modified DNAs were synthesized for the further understanding of the mechanism of charge separation in DNA in order to generate a long-lived charge-separated state with a high quantum yield ( $\Phi$ ). We found that the charge separation process in DNA can be refined by putting a redox inactive intervening base-pair as a spacer between a photosensitizer and the nucleobase to be oxidized to slow down the charge recombination rate.

### **Creation of functional nano-scale biomaterials**

We investigated the arrangement and integration of chromophores using the frames of DNA and proteins and interaction of chromophores incorporated selectively. We successfully obtained the DNA nanostructures which were extended to micro-meter scale using DNA building blocks including the crosslinked DNA and DNA tile system. We also constructed the self-assembled porphyrin structures using the TMV, and investigated the arrangement and energy transfer process. Using these self-assembled structures, we investigate the functional nano-materials, control of the structures and photophysical responses, and the photochemical and electrochemical properties.

### **In-situ photochemical fabrication of metal nanoparticle/polymer composite**

The metal nanoparticle/polymer nanocomposites were fabricated using in-situ photochemical fabrication method. When gold and copper ions were simultaneously reduced by photochemically-produced ketyl radicals in a poly(vinyl alcohol) film, the core/shell structured Au/Cu bimetallic nanoparticles were formed. On the other hand, when co-existing gold and nickel ions were treated by the similar manner, nickel ion was not reduced by ketyl radical and adsorbed on the formed gold nanoparticle.



## Publications

### Original Papers

Single-Molecule Observation of DNA Charge Transfer, T. Takada, M. Fujitsuka, and T. Majima: *Proc. Nat. Acad. Sci. USA*, 104 (27) (2007) 11179-11183.

Intermolecular Electron Transfer from Excited Benzophenone Ketyl Radical, M. Sakamoto, X. Cai, S. S. Kim, M. Fujitsuka, and T. Majima: *J. Phys. Chem. A*, 111 (2) (2007) 223-229.

One-Electron Oxidation of Alcohols by the 1,3,5-Trimethoxybenzene Radical Cation in the Excited State during Two-Color Two-Laser Flash Photolysis, X. Cai, M. Sakamoto, M. Fujitsuka, and T. Majima: *J. Phys. Chem. A*, 111 (10) (2007) 1788-1791.

Bimolecular Hole Transfer from the Trimethoxybenzene Radical Cation in the Excited State, X. Cai, M. Fujitsuka, and T. Majima: *J. Phys. Chem. A*, 111 (22) (2007) 4743-4747.

Intramolecular Triplet Energy Transfer via Higher Triplet Excited State during Stepwise Two-color Two-laser Irradiation, Y. Oseki, M. Fujitsuka, M. Sakamoto, A. Sugimoto, and T. Majima: *J. Phys. Chem. A*, 111 (39) (2007) 9781-9788.

Electron Transfer from Axial Ligand to  $S_1$ - and  $S_2$ -Excited Phosphorus Tetraphenylporphyrin, M. Fujitsuka, D. W. Cho, S. Tojo, A. Inoue, T. Shiragami, M. Yasuda, and T. Majima: *J. Phys. Chem. A*, 111 (42) (2007) 10574-10579.

Electron Transfer from  $S_2$  and  $S_1$  States of Pentacoordinated Tetrapyrrole Macrocycles to Pyromellitic Diimide as an Axial Ligand, K. Harada, M. Fujitsuka, A. Sugimoto, and T. Majima: *J. Phys. Chem. A*, 111 (45) (2007) 11430-11436.

Hole Transfer in DNA and Photosensitized DNA Damage: Importance of Adenine Oxidation, K. Kawai, Y. Osakada, M. Fujitsuka, and T. Majima: *J. Phys. Chem. B*, 111 (9) (2007) 2322-2326.

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Fluorescence Properties of Si-linked Oligothiophenes, M. Fujitsuka, D. W. Cho, J. Ohishita, A. Kunai, and T. Majima: *J. Phys. Chem. C*, 111 (5) (2007) 1993-1998.

Design of Cyclic Reaction Driven by Two-Color Two-Photon Excitation, M. Sakamoto, S. S. Kim, M. Fujitsuka, and T. Majima: *J. Phys. Chem. C (Lett.)*, 111 (19) (2007) 6917-6919.

Correction to "Acceleration and Deceleration of Laser Induced Formation of Gold Nanoparticles in a PVA Film", M. Sakamoto, T. Tachikawa, M. Fujitsuka, and T.

Majima: *Langmuir*, 23 (14) (2007) 7886-7886.

Donor-Acceptor Substituted Tetrakis(phenylethynyl)benzenes as Emissive Molecules during Pulse Radiolysis in Benzene, S. Samori, S. Tojo, M. Fujitsuka, E. L. Spitler, M. M. Haley, and T. Majima: *J. Org. Chem.*, 72 (8) (2007) 2785-2793.

Relationship between Charge Transfer and Charge Recombination Determines Photocurrent Efficiency through DNA Films, T. Takada, C. Lin, and T. Majima: *Angew. Chem. Int. Ed.*, 46 (35) (2007) 6681-6683.

Hole transfer rates in A-from DNA/2'-OMeRNA hybrid, K. Kawai, Y. Osakada, A. Sugimoto, M. Fujitsuka, and T. Majima: *Chem. Eur. J.*, 13 (8) (2007) 2386-2391.

C-O-bond cleavage of esters with a naphthyl group in the higher triplet excited state during two-color two-laser flash photolysis, X. Cai, M. Sakamoto, M. Yamaji, M. Fujitsuka, and T. Majima: *Chem. Eur. J.*, 13 (11) (2007) 3143-3149.

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Spin-correlated radical pairs in the synthetic hairpin DNA, S. Nakajima, K. Akiyama, K. Kawai, T. Takada, T. Ikoma, T. Majima, and S. Tero-Kubota: *ChemPhysChem*, 8 (4) (2007) 507-509.

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Errata to "Two-color Two-laser Fabrication of Gold Nanoparticles in a PVA Film", M. Sakamoto, T. Tachikawa, M. Fujitsuka, and T. Majima: *Chem. Phys. Lett.*, 442 (1-3) (2007) 170.

The C-O bond dissociation of naphthoxymethyl compounds in the higher triplet excited state using two-color two-laser flash photolysis, X. Cai, M. Yamaji, M. Sakamoto, M. Fujitsuka, and T. Majima: *Chem. Phys. Lett.*, 443 (4-6) (2007) 248-252.

Nanoscopic Heterogeneities in Adsorption and Electron Transfer Processes of Perylene Diimide Dye on TiO<sub>2</sub> Nanoparticles Studied by Single-Molecule Fluorescence Spectroscopy, T. Tachikawa, S.-C. Cui, S. Tojo, M. Fujitsuka, and T. Majima: *Chem. Phys. Lett.*, 443 (4-6) (2007) 313-318.

Monitoring G-Quadruplex Structures and G-Quadruplex-ligand Complex by

2-Aminopurine Modified Oligonucleotide, T. Kimura, K. Kawai, M. Fujitsuka, and T. Majima: *Tetrahedron*, 63 (17) (2007) 3585-3590.

S<sub>2</sub>- and S<sub>1</sub>-States Properties of Zinc Porphyrin Polypeptides, M. Fujitsuka, D. W. Cho, N. Solladie, V. Troiani, H. Qiu, and T. Majima: *J. Photochem. Photobiol. A*, 188 (2-3) (2007) 346-350.

Intermolecular Exciplex Formation and Intramolecular Electron Transfer during Photoirradiation of 1,8-Naphthalimide-linker-phenothiazine Dyads in Methylated Benzenes, D. W. Cho, M. Fujitsuka, U. C. Yoon, and T. Majima: *J. Photochem. Photobiol. A*, 190 (1) (2007) 101-109.

Monitoring of Three Distinct Structures of Restriction Enzyme Complexes Using Characteristic Fluorescence from Site-selectively Incorporated Solvatochromic Probe, K. Nakayama, M. Endo, M. Fujitsuka, and T. Majima: *Photochem. Photobiol. Sci.*, 6 (2007) 836-841.

Reversible Intramolecular Triplet-Triplet Energy Transfer in Benzophenone-N-Methylphthalimide Dyad Aprotic Polar and Protic Polar Solvents, M. Sakamoto, S. S. Kim, M. Fujitsuka, and T. Majima: *J. Phys. Chem. A*, 112 (7) (2008) 1403-1407.

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Protein Recording Material: Photo-Record/Erasable Protein Array Using a UV-Eliminative Linker, K. Nakayama, T. Tachikawa, and T. Majima: *Langmuir (Letter)*, 24 (5) (2008) 1625-1628.

Diastereochemically Controlled Porphyrin Dimer Formation on a DNA Duplex Scaffold, M. Endo, M. Fujitsuka, and T. Majima: *J. Org. Chem.*, 73 (3) (2008) 1106-1112.

Three-Dimensional Writing of Copper Nanoparticles in a Polymer Matrix with Two-Colour Two-Laser, M. Sakamoto, T. Tachikawa, M. Fujitsuka, and T. Majima: *J. Org. Chem.*, 73 (9) (2008) 3551-3558.

Photocatalytic Cleavage of Single TiO<sub>2</sub>/DNA Nanoconjugates, T. Tachikawa, Y. Asanoi, K. Kawai, S. Tojo, A. Sugimoto, M. Fujitsuka, and T. Majima: *Chem. Eur. J.*, 14 (5) (2008) 1492-1498.

Mechanism of Charge-Separation in DNA via Hole Transfer through Consecutive Adenines, K. Kawai, Y. Osakada, M. Fujitsuka, and T. Majima: *Chem. Eur. J.*, 14 (12)

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Conformational regulation of porphyrin dimers on geometric scaffold of duplex DNA, M. Endo, M. Fujitsuka, and T. Majima: *Tetrahedron*, 64 (8) (2008) 1839-1846.

### **Review Papers**

Relationship between Charge Transfer in DNA and Information, T. Majima, *Chemistry*, 62[1] (2007) 23-24.

DNA Molecular Chemistry, T. Majima, in "Development of Biomolecule Science", Chemical Society of Japan, 41-45(2007).

Mechanistic Insight into the  $\text{TiO}_2$  Photocatalytic Reactions: Design of New Photocatalysts, T. Tachikawa, M. Fujitsuka, and T. Majima, *J. Phys. Chem. C* (Feature Article), 111[14] (2007) 5259-5275.

Single-Molecule Detection of Reactive Oxygen Species: Application to Photocatalytic Reactions, T. Tachikawa and T. Majima, *J. Fluores.* (Special issue on "Advances in Single Molecule Spectroscopy", invited), 17[6] (2007) 727-738.

Photochemical Properties of Porphyrin-attached Tobacco Mosaic Virus, M. Endo, Fujitsuka, and T. Majima, *Photomedicine and Photobiology*, 29 (2007) 19-20.

DNA Device by Charge Transfer in DNA, T. Majima, *Chemistry*, 63[1] (2008) 38-40.

Charge Transfer in DNA, T. Takada and T. Majima, *Manufacturing and Technology*, 60[1] (2008) 55-60.

Charge Transfer in DNA and its Application to Biosensors, T. Takada and T. Majima, *BIO INDUSTRY*, 25[3] (2008) 61-71.

### **Books**

"Photochemistry of Short-lived Species using Multi-beam Irradiation" "Advanced in Photochemistry Vol 29" (ed by D. C. Neckers, W. Jenks, T. Wolff), M. Fujitsuka and T. Majima, John Wiley & Sons, Inc., (2007) 53-109.

"Single-Molecule Fluorescence Imaging Techniques for the Detection of Reactive Oxygen Species", "Modern Research and Educational Topics on Microscopy" (ed by A. Mendez-Vilas and J. Diaz), T. Tachikawa and T. Majima, Formatex, (2007) 651-659.

"DNA Supramolecular Structures for the Creation of Functional Nanomaterials" "Soft Nanomaterials" (ed by H. S. Nalwa, American Scientific Publishers), M. Endo and T. Majima, Valencia, (2008).

"Single molecule fluorescence imaging in photocatalytic reaction", in "New chemistry world by photon and interface: photocatalyst and photoenergy conversion", T. Majima,

Kuba-pro Co. (2008) 50-58.

### **Patents**

“SNP detection method by DNA single molecule fluorescence measurement based on DNA charge transfer”, T. Majima, T. Takada, K. Kawai, M. Fujitsuka, No. 2007-6829.

“Preparation of metal nanoparticles in matrices”, T. Majima, M. Sakamoto, M. Fujitsuka, No. 2007-28166.

“Preparation of modified metal nanoparticles and its method”, T. Majima, M. Sakamoto, M. Fujitsuka, No. 2007-095031.

### **International Conferences**

Charge Transfer in DNA (invited), T. Majima: 2007 Photochemistry Gordon Research Conference, Bryant University, Smithfield, Rhode Island, USA, July 8-13, 2007.

Mechanistic Insight into the  $\text{TiO}_2$  Photocatalytic Reactions (invited), T. Majima: 23th International Conference on Photochemistry, Cologne, Germany, July 29-Aug. 3, 2007.

Rapid Energy Migration along Photofunctional Polymers (poster), M. Fujitsuka and \*T. Majima: 23th International Conference on Photochemistry, Cologne, Germany, July 29-Aug. 3, 2007.

Charge Separation via Rapid Hole Transfer through Adenine-Hopping (poster), T. Takada, K. Kawai, M. Fujitsuka, and \*T. Majima: 23th International Conference on Photochemistry, Cologne, Germany, July 29-Aug. 3, 2007.

One-electron oxidation of organic compounds during  $\text{TiO}_2$  photocatalytic reactions (invited), \*T. Tachikawa and T. Majima: Langmuir Symposium 2007 in Osaka University, Suita, Japan, Oct. 9, 2007.

Photochemical synthesis of metal nanoparticles in a PVA film (invited), \*M. Sakamoto and T. Majima: Langmuir Symposium 2007 in Osaka University, Suita, Japan, Oct. 9, 2007.

Development of New  $\text{TiO}_2$  Photocatalysts (invited), T. Majima: 7th Pacific Rim Conference on Ceramic and Glass Technology, Shanghai, Nov. 11-14, 2007.

Adsorption and Electron Transfer Processes of Perylene Diimide Dye on  $\text{TiO}_2$  Nanoparticles Studied by Single-Molecule (poster), \*S.-C. Cui, T. Tachikawa, S. Tojo, M. Fujitsuka, T. Majima: 7th Pacific Rim Conference on Ceramic and Glass Technology, Shanghai, Nov. 11-14, 2007.

Possibility of Negative Charge Conduction in Cyclophanes (invited), T. Majima: The Third Taiwan-Japan Bilateral Symposium on Functional Molecules, Janfusen, Taiwan, Nov. 11-14, 2007.

Development of New TiO<sub>2</sub> Photocatalyst: Mechanistic Study of TiO<sub>2</sub> Photocatalytic Reactions (invited), T. Majima: 2007 Korea-Japan Symposium on Frontier Photoscience, Gyeongju, Korea, Nov. 22-25, 2007.

Intramolecular Electron Transfer from Axial Ligands to S<sub>2</sub>-Excited Tetraphenyl Porphyrins (invited), \*M. Fujitsuka and T. Majima: 2007 Korea-Japan Symposium on Frontier Photoscience, Gyeongju, Korea, Nov. 22-25, 2007.

Excited State Properties of Trimethoxybenzene Radical Cation (poster), X. Cai, M. Fujitsuka, and \*T. Majima: 2007 Korea-Japan Symposium on Frontier Photoscience, Gyeongju, Korea, Nov. 22-25, 2007.

Photoinduced Electron Transfer from S<sub>2</sub>-Excited Porphyrins and Phthalocyanines (poster), K. Harada, M. Fujitsuka, and \*T. Majima: 2007 Korea-Japan Symposium on Frontier Photoscience, Gyeongju, Korea, Nov. 22-25, 2007.

Energy Levels of Oligothiophenes in Higher Triplet Excited State (poster), Y. Oseki, M. Fujitsuka, and \*T. Majima: 2007 Korea-Japan Symposium on Frontier Photoscience, Gyeongju, Korea, Nov. 22-25, 2007.

Development of New TiO<sub>2</sub> Photocatalyst: Mechanistic Study of TiO<sub>2</sub> Photocatalytic Reactions (invited), T. Majima: The 9th International Symposium on Eco-materials Processing and Design, Changwon Exhibition Convention Center, Changwon, Korea, Jan. 7-9, 2008.

Photoinduced Charge Separation in Titania Nanotubes (poster), \*T. Tachikawa, S. Tojo, M. Fujitsuka, T. Sekino, and T. Majima: The 9th International Symposium on Eco-materials Processing and Design, Changwon Exhibition Convention Center, Changwon, Korea, Jan. 7-9, 2008.

Single-Molecule Detection of Airborne Singlet Oxygen (poster), \*K. Naito, T. Tachikawa, S.-C. Cui, A. Sugimoto, M. Fujitsuka, and T. Majima: The 9th International Symposium on Eco-materials Processing and Design, Changwon Exhibition Convention Center, Changwon, Korea, Jan. 7-9, 2008.

Charge Separation in Acridine Modified DNA (poster), \*K. Kawai, M. Fujitsuka, and T. Majima: 11th Sanken International Symposium / 6th nanotechnology center international symposium / 1st MSTEC international symposium, Awaji, Japan, Feb. 4-5, 2008.

Kinetic SNP typing Based on Charge Transfer through DNA (poster), Y. Osakada, \*K. Kawai, M. Fujitsuka, and T. Majima: 11th Sanken International Symposium / 6th nanotechnology center international symposium / 1st MSTEC international symposium, Awaji, Japan, Feb. 4-5, 2008.

Intramolecular Electron Transfer from Axial Ligands to S<sub>2</sub>-Excited Tetraphenyl Porphyrins (poster), M. Fujitsuka and \*T. Majima: 11th Sanken International

Symposium / 6th nanotechnology center international symposium / 1st MSTEC international symposium, Awaji, Japan, Feb. 4-5, 2008.

Single-Molecule Detection of Airborne Singlet Oxygen (poster), T. Tachikawa, K. Naito, M. Fujitsuka and \*T. Majima: 11th Sanken International Symposium / 6th nanotechnology center international symposium / 1st MSTEC international symposium, Awaji, Japan, Feb. 4-5, 2008.

Design of Cyclic Reaction Driven by the Two-color Two-photon Excitation (poster), M. Sakamoto, M. Fujitsuka and \*T. Majima: 11th Sanken International Symposium / 6th nanotechnology center international symposium / 1st MSTEC international symposium, Awaji, Japan, Feb. 4-5, 2008.

Molecular Excitation Chemistry of Supramolecules and Nanomaterials, T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Electron Transfer from Axial Ligand to  $S_1$ - and  $S_2$ -Excited Phosphorus Tetraphenylporphyrin, \*M. Fujitsuka, D. W. Cho, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Photophysical Properties of 1,8-Naphthalimide-linker-phenothiazine Dyads in Non-polar Solvents, \*D. W. Cho, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Single Molecule Fluorescence Imaging of  $TiO_2$  Photocatalytic Reactions, \*T. Tachikawa, S. Tojo, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Photochemical Formation of Au/Cu Bimetallic Nanoparticles with Different Shapes and Sizes in a PVA Film, \*M. Sakamoto, T. Tachikawa, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Hole Transfer in DNA and Photosensitized DNA Damage: Importance of Adenine Oxidation, \*K. Kawai, Y. Osakada, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Single-Molecule Observation of DNA Charge Transfer, \*T. Takada, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Porphyrin Light-Harvesting System Constructed in the Tobacco Mosaic Virus Scaffold,

\*M. Endo, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Higher Excited State Chemistry for Light-Energy Conversion (invited), M. Fujitsuka and \*T. Majima: The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science, Daejeon, Korea, Feb. 27-28, 2008.

DNA Devices Based on Charge Transfer in DNA (invited), T. Majima: The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science, Daejeon, Korea, Feb. 27-28, 2008.

### **Contributions to International Conferences and Journals**

|           |                                                                                                                 |
|-----------|-----------------------------------------------------------------------------------------------------------------|
| T. Majima | 2007 KOREA-JAPAN Symposium on Frontier Photoscience (Conference Chair)                                          |
| T. Majima | Symposium on “Beam-induced Chemistry of Supramolecules and Nanomaterials 2007 (Conference Chair)                |
| T. Majima | Langmuir Symposium 2007 in Osaka University (Conference Chair)                                                  |
| T. Majima | The 9 <sup>th</sup> International Symposium on Eco-materials Processing and Design (Organizing Committee)       |
| T. Majima | International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008” (Conference Chair) |
| T. Majima | The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science (Conference Chair)                             |
| T. Majima | Langmuir, American Chemical Society (Senior Editor)                                                             |

### **Publications in Domestic Meetings**

|                                              |           |
|----------------------------------------------|-----------|
| Japan Photobiology and Photomedicine Meeting | 2 papers  |
| Photochemistry Meeting                       | 11 papers |
| Polymer Meeting                              | 1 paper   |
| Japan Chemical Society Meeting               | 10 papers |

### **Academic Degrees**

#### **Doctor Degree of Engineering**

|           |                                                                                                                              |
|-----------|------------------------------------------------------------------------------------------------------------------------------|
| S. Samori | Studies on the Formation and Reactivity of Radical Ions of Aromatic Compounds by Laser Flash Photolysis and Pulse Radiolysis |
|-----------|------------------------------------------------------------------------------------------------------------------------------|

#### **Master Degree for Engineering**

|            |                                                                                                                                                             |
|------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|
| K. Harada  | Electron Transfer from the S <sub>1</sub> and S <sub>2</sub> States of Pentacoordinated Tetrapyrrole Macrocycles to Pyromellitic Diimide as an Axial Ligand |
| H. Urasaki | Conformational change of polypeptides induced by formation of                                                                                               |



|           |                                                                                                                              |
|-----------|------------------------------------------------------------------------------------------------------------------------------|
| C. Lin    | carbazole dimer radical cation<br>Mechanism of Photocurrent Generation through DNA Films<br>Based on Charge Transfer Process |
| S.-C. Cui | Photoexcited Perylenediimide Dye on the Surface of TiO <sub>2</sub><br>Studied by Single-Molecule Fluorescence Spectroscopy  |

## Sponsorship

### Grand-in-Aid for Scientific Research (S)

|           |                                        |             |
|-----------|----------------------------------------|-------------|
| T. Majima | Nanoscience of Photofunctionalized DNA | ¥10,920,000 |
|-----------|----------------------------------------|-------------|

### Grand-in-Aid for Basic Scientific Research

|           |                                                                                                                           |            |
|-----------|---------------------------------------------------------------------------------------------------------------------------|------------|
| T. Majima | Construction of devices for photoelectronic conversion using photochemical control of Tobacco Mosaic Virus supramolecules | ¥1,800,000 |
|-----------|---------------------------------------------------------------------------------------------------------------------------|------------|

### Grand-in-Aid for Scientific Research (B)

|              |                                                               |             |
|--------------|---------------------------------------------------------------|-------------|
| M. Fujitsuka | Studies toward molecular device using femtosecond multi-laser | ¥12,740,000 |
|--------------|---------------------------------------------------------------|-------------|

### Grand-in-Aid for Scientific Research (C)

|         |                                                                                                       |            |
|---------|-------------------------------------------------------------------------------------------------------|------------|
| S. Tojo | Development of novel TiO <sub>2</sub> catalysts modified by polyacids and its multi-excitation effect | ¥1,100,000 |
|---------|-------------------------------------------------------------------------------------------------------|------------|

### Grand-in-Aid for Encouragement of Young Scientists

|              |                                                                                            |            |
|--------------|--------------------------------------------------------------------------------------------|------------|
| T. Tachikawa | Fabrication and Photocatalytic Activity of Nanostructured TiO <sub>2</sub> -DNA Composites | ¥2,400,000 |
|--------------|--------------------------------------------------------------------------------------------|------------|

### Grand-in-Aid for Scientific Research for Young Scientist

|            |                                                                                          |            |
|------------|------------------------------------------------------------------------------------------|------------|
| K. Tainaka | Development of fluorescent molecule-modified nucleobases with the environmental response | ¥1,200,000 |
|------------|------------------------------------------------------------------------------------------|------------|

### Grand-in-Aid for Scientific Research for Young Scientist

|          |                                                                                                    |          |
|----------|----------------------------------------------------------------------------------------------------|----------|
| Y. Oseki | Study on charge transfer via higher triplet state and ultra fast photo-switching molecular devices | ¥900,000 |
|----------|----------------------------------------------------------------------------------------------------|----------|

### Grand-in-Aid for Scientific Research for Young Scientist

|           |                                                                               |            |
|-----------|-------------------------------------------------------------------------------|------------|
| S. Samori | Beam chemical reaction towards high efficient photochemical molecular devices | ¥1,000,000 |
|-----------|-------------------------------------------------------------------------------|------------|

### Grand-in-Aid for Scientific Research for Young Scientist

|            |                                                                                                               |          |
|------------|---------------------------------------------------------------------------------------------------------------|----------|
| Y. Osakada | Study on photoinduced DNA damage caused by charge transfer in DNA toward application to photo dynamic therapy | ¥900,000 |
|------------|---------------------------------------------------------------------------------------------------------------|----------|

### Grand-in-Aid for Scientific Research for Young Scientist

|          |                                                                                                                        |          |
|----------|------------------------------------------------------------------------------------------------------------------------|----------|
| K. Naito | Characterization and application of photo-functionalized carbon nanotube by single molecular fluorescence spectroscopy | ¥900,000 |
|----------|------------------------------------------------------------------------------------------------------------------------|----------|

**Entrusted Research**

|           |                        |                                     |            |
|-----------|------------------------|-------------------------------------|------------|
| T. Majima | IDEC Co.<br>Satake Co. | Selection of plastic by laser light | ¥1,690,000 |
|-----------|------------------------|-------------------------------------|------------|

**Other Research Fund**

|           |            |                                                                             |            |
|-----------|------------|-----------------------------------------------------------------------------|------------|
| T. Majima | TOYOTA Co. | Hydrogen absorbing alloys with high surface area produced by photoreduction | ¥5,989,000 |
|-----------|------------|-----------------------------------------------------------------------------|------------|

|           |                       |                                                                  |          |
|-----------|-----------------------|------------------------------------------------------------------|----------|
| T. Majima | Sekisui Chemicals Co. | Super hydrophilicity by TiO <sub>2</sub> photocatalytic reaction | ¥999,000 |
|-----------|-----------------------|------------------------------------------------------------------|----------|

|           |                                    |                                                                         |            |
|-----------|------------------------------------|-------------------------------------------------------------------------|------------|
| T. Majima | Matsushita Electric Industrial Co. | Study on highly reactive nanostructured TiO <sub>2</sub> photocatalysts | ¥1,732,000 |
|-----------|------------------------------------|-------------------------------------------------------------------------|------------|

|           |                         |                                                               |            |
|-----------|-------------------------|---------------------------------------------------------------|------------|
| T. Majima | Mitsubishi Chemical Co. | Basic research on chemical reaction via higher excited states | ¥2,000,000 |
|-----------|-------------------------|---------------------------------------------------------------|------------|

|              |                                           |  |            |
|--------------|-------------------------------------------|--|------------|
| T. Tachikawa | Iketani Science and Technology Foundation |  | ¥1,500,000 |
|--------------|-------------------------------------------|--|------------|

## Department of Synthetic Organic Chemistry

|                          |                                                                                                                                                                                                                                                                           |
|--------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Professor:               | Hiroaki SASAI                                                                                                                                                                                                                                                             |
| Associate Professor:     | Kiyotaka ONITSUKA                                                                                                                                                                                                                                                         |
| Research Associate:      | Junko ICHIHARA, Doss JAYAPRAKASH                                                                                                                                                                                                                                          |
| Post Doctoral Fellows:   | Gan Bahadur BAJRACHARYA                                                                                                                                                                                                                                                   |
| Research Assistants:     | Kaoru SUZUKI                                                                                                                                                                                                                                                              |
| Graduate Students:       | Tetsuya TSUJIHARA, Rashid Nabisaheb NADAF,<br>Naohito INOUE, Doss RAJESH, Kazem GHOZATI,<br>Yu ITANO, Chiaki KAMEYAMA, Shuhei NAKATSUKA,<br>Shuichi HIRATA, Gabr Randa Kassem MOHAMED,<br>Noriyuki ITOH, Kimiko KIRIYAMA, Kaori TANAKA,<br>Yugo TANIGAKI, Toyohiro NAGANO |
| Research Student:        | Mohanta Suman CHANDRA                                                                                                                                                                                                                                                     |
| Under Graduate Students: | Shintaro HASHIMOTO                                                                                                                                                                                                                                                        |
| Supporting Staff:        | Misuzu TANNO, Miho OHAMA                                                                                                                                                                                                                                                  |

## Outlines

Asymmetric synthesis, a phenomenon fine-tuned to perfection by nature, forms the central theme of our research efforts. We have been interested in the design and syntheses of a novel class of chiral ligands that are unique in promoting new asymmetric reactions. The mechanisms of these organic reactions are also studied by means of physical organic techniques. Novel chiral spiro ionic liquids and organocatalysts have been synthesized with a focus on developing environmentally benign asymmetric processes.

## Current Research Project

### Development of Chiral Bifunctional Organocatalysts

The C–C bond-forming reaction between the  $\alpha$ -position of electron-deficient alkenes and the  $sp^2$  carbon atom of imines in the presence of a suitable nucleophilic catalyst is referred to as the aza-Morita–Baylis–Hillman (aza-MBH) reaction. Since the aza-MBH reaction gives impressively functionalized allyl amine products, which are proved to be valuable building blocks for biologically important compounds and natural products, in an atom-economical manner, it has been recognized as one of the most useful organic transformations. We have developed a novel and powerful bifunctional organocatalyst for the aza-MBH reaction of nitroalkenes with *N*-tosylimine derivatives, (*S*)-3-[2-(4-imidazolyl)phenyl]BINOL. The acid–base moieties act cooperatively as an enzyme-mimetic catalyst to activate both the substrates.

### Asymmetric Oxidative Cyclization Catalyzed by Pd-SPRIX Complexes

We have developed asymmetric catalysis using our original chiral bis(isoxazoline) ligands with spiro[4.4]nonane skeleton (SPRIXs). Thus far it has been found that Pd(II)-SPRIX complexes are quite effective catalysts to promote enantioselective Wacker-type reactions. As an extension of their utility, efficient asymmetric synthesis

of  $\gamma$ -butenolides and 2-pyrrolinones, which were valuable architectural platform for many biologically active substances, was examined. Pd(II)-SPRIX-catalyzed oxidative cyclization of  $\beta,\gamma$ -unsaturated carboxylic acids and  $\beta,\gamma$ -unsaturated amides afforded optically active  $\gamma$ -butenolides and 2-pyrrolinone derivatives, respectively. It is noteworthy that the known chiral ligands did not exhibit any accelerating effects in the above reactions.

#### **Efficient Synthetic Method of Chiral Hybrid Spiro (Isoxazole-Isoxazoline) Ligands**

Development of efficient synthetic method of novel chiral hybrid spiro (isoxazole-isoxazoline) ligands was accomplished. A variety of ligands were readily prepared by palladium-catalyzed coupling reactions of the key intermediate in which bromide was introduced to the 5-position on the isoxazole ring. Their utility as a chiral ligand was examined for palladium-catalyzed oxidative cyclization.

#### **Asymmetric Synthesis of Novel Spiro Bis(isoxazoline) Ligand**

Novel chiral spiro bis(isoxazoline) ligand was prepared without a tedious optical resolution. Diastereoselective intramolecular double nitrile oxide cycloaddition of the key dioxime derived from bis(2,2,2-trifluoroethyl) malonate and the enantiomerically pure alcohol gave the desired ligand.

#### **Catalytic Enantioselective Synthesis of Chiral Spiro lactams**

Enantioselective synthesis of spiro lactams via a palladium-catalyzed intramolecular double Buchwald–Hartwig amidation was investigated. The desired spiro lactams consisting of two 3,4-dihydroquinolinone moieties were obtained in an optically active form by reaction of 2,2-bis(2-bromobenzyl) malonamide derivatives in the presence of palladium catalyst precursor and chiral ligand. Furthermore, the resulting spiro lactams were converted into novel phase transfer catalysts bearing a spiro bis(1,2,3,4-tetrahydroquinoline) framework, which were expected to create effective chiral environment, by conventional synthetic methods such as electrophilic aromatic bromination and hydride reduction.

#### **Stereoselective Reactions with Planar-Chiral Cyclopentadienyl Complexes**

As an extension of our study on asymmetric catalysis of planar-chiral cyclopentadienyl-ruthenium complexes, we examined asymmetric substitution of unsymmetrically substituted allyl derivatives. Reaction of cinnamyl chloride with indole led to the formation of branched allylation product with high region- and enantioselectivities.

#### **Asymmetric Reactions Using Helical Polymers**

One-handed helical polymer is of interest as a chiral source for asymmetric synthesis. We prepared helical polyisocyanide ligands by random copolymerization of chiral achiral monomers, the latter of which had coordination site. The helical polyisocyanide ligands were applied to copper-catalyzed Diels–Alder reaction with moderate enantioselectivity.

#### **Efficient Solvent-free Catalytic Oxidation Using Green Solid-Phase**

We have developed a new approach to solvent-free catalytic oxidation using ‘green

solid-phase'. The solvent-free catalytic oxidation of sulfides proceeds at powdery solid-state by using Keggin phosphomolybdate catalyst ((CetylPy)<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>]) / fluorapatite (Fap) solid-phase with a solid hydrogen peroxide (urea-H<sub>2</sub>O<sub>2</sub>) at rt without stirring. The solid catalyst/Fap was reusable and retained its high catalytic activity and selectivity, although the catalyst was not fixed on the solid-phase. The high efficiency in the reaction was found to be due to a new peroxo species that retains the framework of the parent cluster. The reactions under powder state enable to make use the structural diversity of polyoxometalates as a catalyst.

## Publications

### Original Papers

Synthesis of Novel Spiro Imidazolium Salts as Chiral Ionic Liquids, M. L. Patil, C. V. L. Rao, S. Takizawa, K. Takenaka, K. Onitsuka, H. Sasai: *Tetrahedron*, 63 (51) (2007) 12702-12711.

Development of New Methods towards Efficient Immobilization of Enantioselective Catalysts, S. Takizawa, M. L. Patil, K. Marubayashi, H. Sasai: *Tetrahedron*, 63 (28) (2007) 6512-6528.

Design and Synthesis of Chiral Hybrid Spiro (isoxazole-isoxazoline) Ligands, P. S. Koranne, T. Tsujihara, M. A. Arai, G. B. Bajracharya, T. Suzuki, K. Onitsuka, H. Sasai: *Tetrahedron: Asymmetry*, 18 (8) (2007) 919-923.

Enantioselective Glyoxylate-ene Reaction using a Novel Spiro Bis(isoxazoline) Ligand in Copper Catalysis, K. Wakita, G. B. Bajracharya, M. A. Arai, S. Takizawa, T. Suzuki, H. Sasai: *Tetrahedron: Asymmetry*, 18 (3) (2007) 372-376.

Optical Resolution of Tetra Isopropyl-substituted Spiro Bis(isoxazoline) i-Pr-SPRIX, S. Takizawa, J. Yogo, T. Tsujihara, K. Onitsuka, H. Sasai: *J. Organomet. Chem.*, 692 (1-3) (2007) 495-498.

Novel Azalides Derived from Sixteen-membered Macrolides. I. Isolation of the Mobile Dialdehyde and its One-pot Macrocyclization with an Amine, T. Miura, S. Natsume, K. Kanemoto, K. Atsumi, H. Fushimi, H. Sasai, T. Arai, T. Yoshida, K. Ajito: *J. Antibiot.*, 60 (7) (2007) 407-435.

Chiral Dinuclear Vanadium(V) Catalysts for Oxidative Coupling of 2-Naphthols, S. Takizawa, T. Katayama, C. Kameyama, K. Onitsuka, T. Suzuki, T. Yanagida, T. Kawai, H. Sasai: *Chem. Commun.*, (15) (2008) 1810-1812.

Dual Activation in Oxidative Coupling of 2-Naphthols Catalyzed by Chiral Dinuclear Vanadium Complexes, S. Takizawa, T. Katayama, H. Somei, Y. Asano, T. Yoshida, C. Kameyama, D. Rajesh, K. Onitsuka, T. Suzuki, M. Mikami, H. Yamataka, D. Jayaprakash, H. Sasai: *Tetrahedron*, 64 (15) (2008) 3361-3371.

Control of Helical Structure in Random Copolymers of Chiral and Achiral Aryl

Isocyanides Prepared with Palladium–Platinum  $\mu$ -Ethynediyl Complexes, F. Takei, K. Onitsuka, S. Takahashi, K. Terao, T. Sato: *Macromolecules*, 40 (15) (2007) 5245-5254.

Two- and Three-Dimensional Smectic Ordering of Single-Handed Helical Polymers, H. Onouchi, K. Okoshi, T. Kajitani, S. Sakurai, K. Nagai, J. Kumaki, K. Onitsuka, E. Yashima: *J. Am. Chem. Soc.*, 130 (1) (2008) 229-236.

Organoruthenium Dendrimers Possessing Tris(4-ethynylphenyl)amine Bridges, K. Onitsuka, N. Ohara, F. Takei, S. Takahashi: *Organometallics*, 27 (1) (2008) 25-27.

Regio- and Enantioselective O-Allylation of Phenol and Alcohol Catalyzed by Planar-Chiral Cyclopentadienyl-Ruthenium Complex, K. Onitsuka, H. Okuda, H. Sasai: *Angew. Chem. Int. Ed.*, 47 (8) (2008) 1454-1457.

Characteristics of apatites as a disperse phase for solid-phase organic oxidation system, K. Iteya, Y. Sasaki, M. Iwasaki, S. Ito, J. Ichihara: *J. Ceram. Process. Res.*, 8 (2007) 38-42.

Characteristics of apatite solid disperse phase materials for solvent-free reaction, K. Iteya, Y. Sasaki, M. Iwasaki, S. Ito, J. Ichihara: *Material Technology*, 25 (2007) 17-23.

### **Review Papers**

Bifunctional Organocatalysts for Enantioselective aza-Morita–Baylis–Hillman (aza-MBH) Reactions, S. Takizawa, K. Matsui, H. Sasai: *J. Synth. Org. Chem. Jpn.*, 65 [11] (2007) 1089-1098.

Environmentally Benign Solvent-free Catalytic Reaction Using Fluoroapatite (in Japanese), J. Ichihara, *Materials Science and Technology*, 44 [4] (2007) 157-162.

Recent Development on Chiral Ionic Liquids: Design, Synthesis, and Applications, M. L. Patil, H. Sasai, *The Chemical Record* 8[2] (2008), 98-108.

### **Books**

Asymmetric Phase Transfer Catalysis, H. Sasai, M. L. Patil, Wiley-VCH, (2008) 135-159.

### **Patents**

Solid-phase Oxidation System, J. Ichihara, S. Yamaguchi, JP2007-022073.

### **International Conferences**

Development of New Catalytic Enantioselective Reactions Promoted by Pd(II)-Spiro Bis(isoxazoline) Complexes (poster), \*G. B. Bajracharya, P. S. Koranne, M. L. Patil, C. V. L. Rao, T. Tsujihara, S. Takizawa, T. Suzuki, H. Sasai: 19th French-Japanese Symposium on Medicinal and Fine Chemistry (FJS-2007), Toyama, Japan, May 13-16, 2007.

Pd(II)-SPRIX-Catalyzed Enantioselective Intramolecular Cyclizations (poster), \*G. B. Bajracharya, M. L. Patil, P. S. Koranne, C. V. L. Rao, T. Tsujihara, T. Suzuki, H. Sasai: 14th IUPAC Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS 14), Nara, Japan, August 2-6, 2007.

Development of Dendritic Artificial Enzymes with Catechol Oxidase Activity (poster), D. Jayaprakash, \*R. N. Nadaf, T. Kawase, T. Suzuki, H. Sasai: 12th Asian Chemical Congress, Kuala Lumpur, Malaysia, August 22-25, 2007.

Development of Dendritic Artificial Enzymes with Catechol Oxidase Activity (poster), \*D. Jayaprakash, R. N. Nadaf, T. Kawase, T. Suzuki, H. Sasai: Chirality at the Nanoscale, Barcelona, Spain, September 17-21, 2007.

Development of New Catalytic Enantioselective Reactions Promoted by Pd(II)-Spiro Bis(isoxazoline) Complex (poster), G. B. Bajracharya, P. S. Koranne, M. L. Patil, C. V. L. Rao, T. Tsujihara, S. Takizawa, T. Suzuki, \*H. Sasai: Chirality at the Nanoscale, Barcelona, Spain, September 17-21, 2007.

Development of New Catalytic Enantioselective Reactions Promoted by Pd(II)-Spiro Bis(isoxazoline) Complexes (poster), \*Y. Tanigaki, G. B. Bajracharya, P. S. Koranne, C. V. L. Rao, M. L. Patil, T. Tsujihara, K. Takenaka, S. Takizawa, K. Onitsuka, H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Development of Novel Chiral Spiro-type Ligands (poster), \*S. Nakatsuka, T. Nagano, P. S. Koranne, K. Takenaka, S. Takizawa, T. Suzuki, K. Onitsuka, H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Development of Dendritic Artificial Enzymes with Catechol Oxidase Activity (poster), \*R. N. Nadaf, D. Jayaprakash, T. Kawase, R. K. M. Gabr, S. Hashimoto, M. Mikami, T. Suzuki, H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Development of Dendritic Artificial Enzymes with Catechol Oxidase Activity (poster), \*S. Hashimoto, R. N. Nadaf, D. Jayaprakash, T. Kawase, G. R. K. Mohamed, M. Mikami, T. Suzuki, H. Sasai: 11th Sanken, 6th Nanotechnology Center, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Bifunctional Chiral Organocatalysts for the Enantioselective aza-Morita-Baylis-Hillman Reaction, \*H. Sasai: 21st International Congress for Heterocyclic Chemistry, Sydney, Australia, July 15-20, 2007.

Development of Bifunctional Organocatalysts for Enantioselective Aza-Morita-Baylis-Hillman Reaction (invited), \*H. Sasai: First International Conference on Advanced Organic Synthesis Directed toward the Ultimate Efficiency and Practicability, International Conference on Asymmetric Organocatalysis, Otsu, Japan, May 28-29, 2007.

Novel Enantioselective Reactions Promoted by Pd(II)-SPRIX Catalyst (invited), \*H. Sasai: International Chemical Conference (ICCT-2007), Hsinchu, Taipei, December 13-16, 2007.

Dual Activation in Oxidative Coupling of 2-Naphthols Catalyzed by Chiral Dinuclear Vanadium Complexes (invited), \*H. Sasai: Post-symposium of ICCT-2007, Hsinchu, Taipei, December 17, 2007.

Dual Activation Catalysis (invited), \*H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Regio- and Enantioselective O-Allylation of Phenol and Alcohol Catalyzed by Planar-Chiral Cyclopentadienyl-Ruthenium Complex (poster), \*K. Onitsuka, H. Okuda, C. Kameyama, H. Sasai: 14th IUPAC Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS 14), Nara, Japan, August 2-6, 2007.

Organoruthenium Dendrimers Possessing Tri(4-Ethynylphenyl)Amine Bridges (poster), \*K. Onitsuka, S. Takahashi: 12th IUPAC International Symposium on Macromolecular Complexes, Fukuoka, Japan, August 27-31, 2007.

Development of New Catalytic Asymmetric Reaction Using Helical Polymer (poster), \*Y. Itano, K. Onitsuka, H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Asymmetric Catalysis of Planar-Chiral Cyclopentadienyl-Ruthenium Complexes: Regio- and Enantioselective Allylic Substitutions (poster), \*K. Onitsuka, H. Okuda, C. Kameyama, H. Sasai: 11th Sanken, 6th Nanotechnology Center, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Design of Novel Helical Polymer Ligands and Their Application to Asymmetric Diels-Alder Reaction (poster), \*K. Onitsuka, Y. Itano, H. Sasai: 11th Sanken, 6th Nanotechnology Center, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Synthesis of Optically Active Spiro Compounds via Palladium-catalyzed Asymmetric Amidation (poster), \*N. Itoh, K. Takenaka, H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Synthesis of Optically Active Spiro Compounds via Palladium-catalyzed Asymmetric Amidation (poster), \*N. Itoh, K. Takenaka, H. Sasai: 11th Sanken, 6th Nanotechnology Center, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

#### **Contributions to International Conferences and Journals**

H. Sasai                      14th IUPAC Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS 14), (Organizing



Committee)

### **Publications in Domestic Meetings**

|                                       |           |
|---------------------------------------|-----------|
| The Chemical Society of Japan         | 13 papers |
| Symposium on Organic Reaction         | 2 papers  |
| Symposium on Organometallic Chemistry | 1 paper   |
| Catalysis Society of Japan Meeting    | 1 paper   |
| Symposium on Macromolecules           | 1 paper   |
| Symposium on Organic Synthesis        | 1 paper   |

### **Academic Degrees**

#### **Master Degree for Science**

|                           |                                                                                                                       |
|---------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Y. Itano                  | Syntheses of Helical Polyisocyanide Ligands Possessing Pyridyl Pendants and Their Application to Asymmetric Catalysis |
| C. Kameyama               | Asymmetric Allylation of Indole Catalyzed by Planar-Chiral Cyclopentadienyl-Ruthenium Complex                         |
| S. Nakatsuka              | Development of Efficient Synthetic Method of Chiral Hybrid Spiro (Isoxazole–Isoxazoline) Ligands                      |
| Gabr Randa Kassem Mohamed | Development of Dendritic Artificial Enzymes                                                                           |

### **Sponsorship**

#### **Grant-in-Aid for Scientific Research on Priority Areas**

|             |                                                                                               |            |
|-------------|-----------------------------------------------------------------------------------------------|------------|
| H. Sasai    | Development of Chiral Organocatalyst with Synergistic Effect                                  | ¥2,300,000 |
| K. Onitsuka | Synthesis and Properties of Hybrid-type of Organometallic Conjugated Polymers                 | ¥1,400,000 |
| K. Onitsuka | Development of Enantioselective Reactions Catalyzed by Planar-Chiral Organometallic Complexes | ¥2,000,000 |

#### **Grant-in-Aid for Scientific Research (C)**

|             |                                                                                        |          |
|-------------|----------------------------------------------------------------------------------------|----------|
| J. Ichihara | Solvent-free Catalytic Oxidation System on Environmentally Benign Solid-disperse-phase | ¥800,000 |
|-------------|----------------------------------------------------------------------------------------|----------|

#### **Entrusted Research**

|          |                                     |                                                                                                             |            |
|----------|-------------------------------------|-------------------------------------------------------------------------------------------------------------|------------|
| H. Sasai | Japan Science and Technology Agency | Preparation of Novel Medicinal Intermediates Based on Enantioselective Reactions Using Chiral Spiro Ligands | ¥2,600,000 |
|----------|-------------------------------------|-------------------------------------------------------------------------------------------------------------|------------|

#### **Other Research Fund**

|          |                                       |                                                                         |            |
|----------|---------------------------------------|-------------------------------------------------------------------------|------------|
| H. Sasai | Hosokawa Powder Technology Foundation | Development of Efficient Synthetic Methods for Functional Nanoparticles | ¥1,000,000 |
| H. Sasai | Meiji Seika Kaisha                    |                                                                         | ¥1,000,000 |
| H. Sasai | Daiso Co.                             |                                                                         | ¥600,000   |
| H. Sasai | Nissan Chemical Industries            |                                                                         | ¥400,000   |
| H. Sasai | Nagase ChemteX Co.                    |                                                                         | ¥200,000   |

## **Department of Analytical Molecular Chemistry**

Professor: Nobuo KATO  
Assistant Professors: Yoshio TAKAI, Shunro Yamaguchi, Kunihiro KAIHATSU,  
Kaori ASANO, Fumie TAKEI  
Post Doctoral Fellow: Shuichi MORI

### **Outlines**

The department of analytical molecular chemistry was newly founded in April 2004. The department is intended to study current analytical molecular chemistry based on the theory, methodology, and techniques about important subjects on molecular chemistry, material chemistry, life science, and environmental chemistry. Researchers in this Department carry out their own researches as well in cooperation with other Departments of the Institute. The department partly contributes to supporting work of Materials Analysis Center of ISIR.

### **Current Research Project**

#### **Regulation of DNA Transcription by Constructing Artificial Bulb Structure with Light Controllable Antisense Molecules**

Construction of bulb structure within chromosomal DNA is a key step at the transcription initiation. We aimed to regulate transcription by constructing an artificial bulb structure with light controllable antisense molecule, which recognizes DNA promoter sequence and unwind the duplex by visible light irradiation. By collaborating with the Department of Organic Fine Chemicals, we synthesized a series of novel azobenzenes that exhibit trans-to-cis photoisomerization under visible light. These azobenzenes were introduced into peptide nucleic acid (PNA), a nucleic acid analogue. Irradiation of visible light to PNA-azobenzene conjugates (PNA-AZO) induced their conformational changes by the isomerization of azobenzene. PNA-AZO recognized duplex DNA in a sequence-specific manner. We are developing a method to construct artificial bulb structure within duplex DNA for regulating transcription using light controllable PNA-AZO.

#### **Inhibition of Influenza Virus Infection by Novel tea Catechin Derivatives**

A series of fatty acid monoester derivatives of (–)-epigallocatechin-3-O-gallate (EGCG), a major green tea catechin, were prepared by one-pot lipase-catalyzed transesterification. The introduction of long alkyl chains was found to enhance the anti-influenza virus activity 24-fold relative to native EGCG. By collaborating with Department of Organic Fine Chemicals and Research Institute of Microbial Diseases in Osaka University, we confirmed that EGCG-monoesters interfered virus-cell membrane fusion step at the early stage of the virus infection. Their unique anti-influenza activity can be useful for treating oseltamivir-resistant virus strains, such as avian influenza.

#### **Fluorescent Detection of Single Nucleotide Difference using Cytosine Bulge Hairpin Primers**

The technique for promptly detecting the genetic mutation is expected as a basis technology that supports the personalized medicine. In this laboratory, we have proposed the technology for genetic mutation detection that uses a small molecule binding to the mismatch and the bulge structure in the duplex DNA. The practical technology must be handy, accurate, and cheap in cost. To meet this demand, we did not study the chemical modification of DNA, but used the molecule selectively binding to the cytosine bulge. Upon binding to cytosine bulge, the fluorescence wavelength shifted the long wavelength by 30 nm. By using this characteristic fluorescence, we have studied to develop the method detecting single nucleotide polymorphisms. A primer having a cytosine bulge site in a hairpin structure and SNP recognition site at the end of 3' was prepared for PCR. Using this primer and fluorescent molecules, allele specific PCR was monitored in order to do SNP typing. As a result of having performed PCR with a template, a big difference was observed for a change of the fluorescence in a difference of a single base at 3' end of primer and succeeded in recognizing a difference of single nucleotide polymorphisms.

## **Publications**

### **Original Papers**

Allele Specific C-Bulge Probes with One Unique Fluorescent Molecule Discriminate the Single Nucleotide Polymorphism in DNA, F. Takei, H. Suda, M. Hagihara, J. Zhang, A. Kobori, and K. Nakatani, *Chem. Eur. J.* 13 (2007) 4452-4457.

Emission of characteristic fluorescence from the ligand-cytosine complex in U<sub>A</sub>/ACU bulged RNA duplex, J. Zhang, F. Takei, and K. Nakatani, *Bioorg. Med. Chem.* 15 (2007) 4813-4817.

Control of Helical Structure in Random Copolymers of Chiral and Achiral Aryl Isocyanides Prepared with Palladium-Platinum  $\mu$ -Ethynediyl Complexes, F. Takei, K. Onitsuka, S. Takahashi, K. Terao, and T. Sato, *Macromolecules* 40 (2007) 5245-5254.

### **Review Papers**

Visiting laboratories in abroad, K. Kaihatsu, *Kagaku (Kagakudojin)*, 63 (2007) 45-48.

### **Patents**

Silver  $\beta$ -ketocarboxylate, metallic silver manufacturing material thereof, and application of silver thereof, S. Katsuaki, S. Yamaguchi, and M. Hatamura, *PCT Int. Appl.* (2007), WO 2007004437.

Membrane fusion inhibitors, K. Kaihatsu, S. Mori, T. Daidoji, S. Miyake, and N. Kato, JP2008-023196.

Anti-cancer agents using acyl derivatives of Epigallocatechin gallate, K. Matsumura, K. Kaihatsu, S. Mori, S.-H. Hyon, JP2007-239955.

### **International Conferences**

Synthesis and Evaluation of VIS-Sensitive Azobenzene Derivatives for Controlling

Cellular Gene Expressions, \*K. Kaihatsu, S. Sawada, and N. Kato, 11th Sanken International Symposium, Awaji, Japan, February 2-4, 2008.

Synthesis of Green Tea Catechin Derivatives and Evaluation of Their Anti-influenza Virus Activity, \*S. Mori, S. Miyake, K. Kaihatsu, and N. Kato, 11th Sanken International Symposium, Awaji, Japan, February 2-4, 2008.

Application for the Fluorescent Detection of Single Nucleotide Difference using Cytosine Bulge Hairpin Primers, \*F. Takei, M. Hagihara, Y. Oka, and K. Nakatani, 11th Sanken International Symposium, Awaji, Japan, February 2-4, 2008.

#### **Publications in Domestic Meetings**

|                                                          |          |
|----------------------------------------------------------|----------|
| The Chemical Society of Japan                            | 3 papers |
| Meeting of West Japan Branches of Japan Chemical Society | 2 papers |
| The Pharmaceutical Society of Japan                      | 1 paper  |
| Japanese Society for Biomaterials                        | 1 paper  |
| Symposium on the Chemistry of Biocatalysis               | 1 paper  |
| Bio-Optics Research Meeting                              | 1 paper  |
| SORST Joint Symposium                                    | 1 paper  |
| Others                                                   | 1 paper  |

#### **Sponsorship**

##### **Grant-in-Aid for Scientific Research (C)**

|          |                                                               |            |
|----------|---------------------------------------------------------------|------------|
| F. Takei | Development of SNP detection method with modified PCR primers | ¥1,820,000 |
|----------|---------------------------------------------------------------|------------|

##### **Grant-in-Aid for Young Scientists (B)**

|             |                                                                                                                         |            |
|-------------|-------------------------------------------------------------------------------------------------------------------------|------------|
| K. Kaihatsu | Construction of artificial DNA bulb structure and regulation of transcription by light controllable antisense molecules | ¥1,900,000 |
|-------------|-------------------------------------------------------------------------------------------------------------------------|------------|

##### **Entrusted Research**

|             |                                                                |                                                                                                |             |
|-------------|----------------------------------------------------------------|------------------------------------------------------------------------------------------------|-------------|
| K. Kaihatsu | NEDO (Industrial technology research and development projects) | Development of Screening Systems for Anti-RNA Virus Drugs Using Novel Tea Catechin Derivatives | ¥22,701,900 |
|-------------|----------------------------------------------------------------|------------------------------------------------------------------------------------------------|-------------|

##### **Other Research Fund**

|             |                       |                                                                                          |            |
|-------------|-----------------------|------------------------------------------------------------------------------------------|------------|
| K. Kaihatsu | Taiyo Kagaku Co., Ltd | Developing functional materials with food components by electrolytic spinning technology | ¥1,000,000 |
|-------------|-----------------------|------------------------------------------------------------------------------------------|------------|

# Division of Intelligent Systems Science

## Outline

The advent of the digital society where tremendous amount of information is electronically accessible has brought the intelligent information processing technologies indispensable. This division, consisting of four departments, challenges the task of computerizing the intelligent human information processing capability to help solve difficult engineering problems and assist intellectual activities. The major research targets include ontology engineering and knowledge reuse/sharing (Knowledge Systems Dept.), use of multi-dimensional information sources and their multi-purpose processing (Intelligent Media Dept.), human-computer interfaces and agents (Architecture for Intelligence Dept.) and data mining, knowledge discovery and machine learning (Advanced Reasoning Dept.). While pursuing its own research target, each department works closely together to similar problems from different perspectives. The division as a whole collaborates with other divisions in the institute by providing the tools we have developed to help them solve their problems and also is benefited by the feedback to open up new research frontiers.

## Achievement

- Theory of role and distributed ontology development environment
- Systematization of functional knowledge using ontological engineering and its deployment
- Release of OMNIBUS: Ontology of learning/instructional theories and theory- and standards-aware authoring system
- Analysis of collaborative learning interaction and meta-cognitive skill modeling
- Enhancement of the methodology of mobile user models for task-oriented mobile service navigation
- Creation of novel sensors
- 3D modeling and visualization
- Medical image analysis
- Omnidirectional surveillance system and human behavior analysis
- Predicate Invention
- Introducing sensors to constructive adaptive user interfaces
- Adaptive agents
- Adaptive Intelligent Tutoring Systems
- Web summarization
- Construction of sensor networks
- Knowledge discovery from extremely high dimensional dynamics data
- Development of basic principles to derive large scale and frequent substructure co-occurrences
- Development of basic principle to derive frequent graph sequences
- Knowledge discovery from large scale similarity data

## Department of Knowledge Systems

|                          |                                                                                   |
|--------------------------|-----------------------------------------------------------------------------------|
| Professor:               | Riichiro MIZOGUCHI                                                                |
| Associate Professor:     | Yoshinobu KITAMURA                                                                |
| Assistant Professor:     | Munehiko SASAJIMA                                                                 |
| Specially Appointed      |                                                                                   |
| Assistant Professors:    | Yusuke HAYASHI, Hiroko KOU (2007.8.1-),<br>Jun ZHOU (2007.9.1-)                   |
| Graduate Students:       | Shinya TARUMI, Seiji ISOTANI, Masanori OOKUBO,<br>Satoshi ENDO, Koichiro FURUTANI |
| Research Student:        | Meng SHUAI((2007.9.1-)                                                            |
| Under Graduate Students: | Sho SEGAWA, Takeru HIROTA                                                         |
| Supporting Staff:        | Naomi BANO                                                                        |

### Outlines

Information science has developed into knowledge science which is expected to play critical roles in the advanced information processing in this new century. In the real world, tiny computers of the higher performance have been used by ordinary people in their homes where they also enjoy access to vast amount of information sources scattered all over the world thanks to the internet. In academic society, on the other hand, the research on artificial intelligence is changing from building stand-alone machines which try to solve problems by themselves to building intelligent partners which augment human capability of problem solving. This division has been run under the philosophy that it contributes not only to the promotion of knowledge science but also to prosperity of the real world by the feedback of the research results to it in the information era. The major topic here is to investigate Ontological Engineering to establish basic theories and technologies for the next-generation knowledge science. The current research projects include: methodology for ontology development and its support environment based on basic theories of ontological engineering, creative design work bench and advanced diagnostic systems based on knowledge systematization, knowledge sharing and reuse, intelligent educational/training systems, and ontology-aware authoring systems.

### Current Research Project

#### 1. Ontology: Theoretical Foundation of Knowledge Engineering

The research on knowledge-based systems aims at making computer systems more intelligent by mimicking intellectual capability of human. The key to achievement of this goal is the fluent knowledge-level communication between humans and computers. The current state of the art of knowledge engineering, however, has not been matured enough to realize it. Considerable amount of meaning of the concepts in human mind is lost in most of the existing knowledge-based systems. This is the major cause of the difficulty of knowledge reuse and sharing and the too strict behavior of the systems for users to feel comfortable. Thus, new theoretical foundation for knowledge engineering is badly needed in knowledge engineering fields. The research on ontology engineering

is one of the most promising approaches to establishment of the foundation. We theorized about the fundamental issues on ontology from both scientific and engineering viewpoints. As a result, we published three enlightening papers which describe drawbacks of the current research, importance of ontological engineering, definitions of an ontology, its functions and roles, its classification and research topics. We further published some research results based on ontological engineering to show concrete examples of a new research direction. One of the most remarkable achievements is a book on “Ontological Engineering” has been published from Ohm-sha Ltd. In January, 2005 which is the first book on the topic in Japan. HOZO, an environment for ontology building/utilization, has been augmented to make it a usable tool by revising its GUI and reimplementation of some functions. It has been extended to cope with distributed development of a large ontology and to improve the compliance with the WWW standards. In 2007, we developed a mapping tool for enabling viewpoint-specific overview of ontologies to help domain experts better understand the target world across domains. We have started building comprehensive ontologies for medicine and genomics in the collaboration with experts of the respective domains. Concerning theoretical issues, further refinement of Role theory and reconsideration on the ontological theory of objects, processes and events have been done aiming at fundamental contribution of ontology theory.

## **2. Systematization of Functional Design Knowledge**

In the engineering domain, the importance of knowledge sharing among designers has been widely recognized. Although advancement of computer technologies has enabled easy access to objective information such as structural information using CAD without designer’s intention, it is difficult to share conceptual engineering knowledge about functionality that can represent designer’s intention so-called design rationales, because there is neither rich common vocabulary for representing functionality of devices nor well-established ontological commitment for capturing such knowledge. The main goal of this research is to promote sharing of the conceptual engineering knowledge about functionality by providing a conceptual framework enabling systematic description of the functional knowledge. We have developed an ontological framework for its modeling including layered ontologies, which provides rich concepts for describing consistent and reusable knowledge. The framework has been deployed successfully in a manufacturing company. Moreover, based on extensions of the ontological framework, a semantic search system for technical documents has been developed and integration of fault knowledge has been realized. In 2007, we developed a mapping between functional taxonomies based on a reference ontology of function and then extended the search system based on the mapping. Next, aiming at clearer semantics of the functional ontologies, we implemented our functional ontology in the standardized ontology language OWL. Furthermore, we developed a functional knowledge externalization and sharing tool named OntoGear based on an advanced XML technology in the collaborative research with the Materials Science and Technology Research Center.

## **3. Methodology for Building Learning Support Systems**

The goal of research on intelligent educational systems is to implement the intellectual capability of human teachers on computer systems. Huge efforts have been devoted to the research for the last two decades. However, the research field has not been growing



methodologically because of lack of theoretical foundation. Ontology is expected to be a firm basis for knowledge engineering, on top of which we can accumulate our knowledge about the principled methodologies to build sharable and reusable knowledge bases. Especially, task ontology, which captures the inherent conceptual structure of problem solving, works as a bridge to fill the conceptual gap between humans and computers during the process of building and using knowledge-based systems. It keeps up the correspondence between the conceptual structure in human mind and the functional structure of knowledge-based systems. In this research project, we have investigated the essential structure of a variety of educational tasks in detail and built educational task ontology. Furthermore, with the aid of the task ontology built, we have developed a sophisticated authoring tool (intelligent educational system development environment) for substation operator training. The recent results include a proposal of Ontology-Awareness aiming at marriage of learning and educational theories and technology. Based on the proposal, we have realized an ontology-aware authoring environment. We have developed authoring task ontology and an architecture of an evolving authoring tool based on the task ontology together with an authoring system for the collaborative learning and an innovative model of meta-cognitive skills with a framework based on the model. The latest achievements include the following; 1) development of a comprehensive ontology of Education of Informatics in high school and a prototype of an intelligent and dynamic authoring support multi-agent system based on the ontology, 2) design of paper-writing training system based on our innovative model of meta-cognitive skills, 3) update of a learning and instructional theory ontology named OMNIBUS and public release of a prototype of theory-aware and standard-compliant authoring tool named SMARTIES based on the ontology, and 4) investigation into the effectiveness of our collaborative learning theory ontology in collaborative learning design through the experiments with real instructors.

#### **4. Task Ontology-based Framework for Mobile Internet Services**

We can get many kinds of mobile services via mobile handsets today. On the other hand, a large number of services cause difficulties in searching, finding and selecting suitable services for consumer's needs. Users have to learn the menu system to access the services; hierarchical structure of the menu, relation between name of the category and services in the category. To solve this problem this project aims at realization of task-oriented menu which is more efficient for retrieving information. By task, we mean users' problem solving activity in the real world. In the task oriented menu, the users seek for services by the name of the directory which represents a task they are involved in rather than the name of category which might be unfamiliar to them. Users select a menu that is most resemble to what they want to do; "get on the train", "draw cash", for example. It has potential of providing useful information for mobile service users quicker than that of a domain-oriented menu today. Value of information depends on the quality of contextual information that contains. You seek for information when you face a trouble, which is difficult to get over with knowledge at hand, on your way of achieving a task. Such a situation is the context and origin of the necessity for the information. In this research project, we have been developing a task ontology-based modeling framework for mobile service navigation. We applied our modeling framework for prototyping a task-oriented menu system with real-scale mobile internet services. We also modified ontologies behind the model. We prepared for evaluation of

our system including usability, ontology and feasibility.

## **Publications**

### **Original Papers**

A Support for Searching Lesson Plans Which Aim at Enhancement of Problem-Solving Ability by Using Metadata Described based on Ontologies, T. Kasai, H. Yamaguchi, K. Nagano and R. Mizoguchi: Japan Journal of Educational Technology, 31 (3) (2007) 337-348.

The Model of Roles within Ontology Development Tool: Hozo, R. Mizoguchi, E. Sunagawa, K. Kozaki and Y. Kitamura: J. of Applied Ontology, 2 (2) (2007) 159-179.

A Semantic Web System for Supporting Teachers Using Ontology Alignment, T. Kasai, H. Yamaguchi, K. Nagano and R. Mizoguchi: Int. J. Metadata, Semantics and Ontologies, 2 (1) (2007) 35-44.

Development of a System for Capturing Design Rationale with Integration of Dynamic Knowledge Management, M. Takeuchi, Y. Koji, Y. Kitamura, Y. Hayashi, M. Ikeda, R. Mizoguchi: Transactions of the Japanese Soc. for Artificial Intelligence, 22 (3) (2007) 263-275.

Interoperability-oriented Integration of Failure Knowledge into Functional Knowledge and Knowledge Transformation based on Concepts Mapping, Y. Koji, Y. Kitamura, Y. Kato, Y. Tsutsui and R. Mizoguchi: Transactions of the Japanese Soc. for Artificial Intelligence, 22 (1) (2007) 78-92.

Multi-Lingual Communication via the Global Communicator - Analyzing Speaker Utterances and Suggesting Potential Replies -, M. Sasajima, K. Imoto, T. Shimomori, N. Yamanaka, M. Yajima, Y. Fukunaga and Y. Masai: Journal of Information Processing Society of Japan, 48 (3) (2007) 1262-1273.

Development of a Design Supporting System for Nano-Materials based on a Framework for Integrated Knowledge of Functioning-Manufacturing Process, S. Tarumi, K. Kozaki, Y. Kitamura, H. Tanaka and R. Mizoguchi: Transactions of the Japanese Soc. for Artificial Intelligence, 23 (1) (2008) 36-49.

### **Review Papers**

Ontological Engineering Approach to Intelligent Support for Human Activities, Yusuke Hayashi and Riichiro Mizoguchi: Journal of Human Interface Society, 9, No. (4) (2007) 275-280.

### **International Conferences**

Development of a Design Supporting System for Nano-Materials based on a Framework for Integrated Knowledge of Functioning-Manufacturing Process, \*S. Tarumi, K. Kozaki, Y. Kitamura, H. Tanaka and R. Mizoguchi: The 10th IASTED International Conference Intelligent Systems and Control(ISC2007),Cambridge, Massachusetts, USA,

Nov. 19-21, 2007.

A Framework for Cooperative Ontology Construction Based on Dependency Management of Modules, \*K. Kozaki, E. Sunagawa, Y. Kitamura and R. Mizoguchi: International Workshop on Emergent Semantics and Ontology Evolution (ESOE2007), Busan, Korea, Nov. 12, 2007.

Towards a Reference Ontology for Functional Knowledge Interoperability, \*Y. Kitamura, S. Takafuji, R. Mizoguchi: ASME International Design Engineering Technical Conferences & Computers and Information in Engineering Conference (ASME2007), Las Vegas, Nevada, USA, Sep. 4-7, 2007.

Towards Interoperability between Functional Taxonomies Using an Ontology-based Mapping, \*M. Ookubo, Y. Koji, M. Sasajima, Y. Kitamura and R. Mizoguchi: The 16th International Conference on Engineering Design (ICED '07), Paris, France, Aug. 28-31, 2007.

Role Representation Model Using OWL and SWRL, \*K. Kozaki, E. Sunagawa, Y. Kitamura and R. Mizoguchi: 2nd Workshop on Roles and Relationships in Object Oriented Programming, Multiagent Systems, and Ontologies, Berlin, July 30-31, 2007.

Distributed and Collaborative Construction of Ontologies Using Hozo, \*K. Kozaki, E. Sunagawa, Y. Kitamura and R. Mizoguchi: Workshop on Social and Collaborative Construction of Structured Knowledge, Banff, Canada, May 8, 2007.

Inside Theory-Aware and Standards-Compliant Authoring System (invited), \*R. Mizoguchi, \*Y. Hayashi and J. Bourdeau: The Fifth International Workshop on Ontologies and Semantic Web for E-Learning (SWEL'07), Marina del Rey, CA, USA, July 9, 2007.

The Unfolding of Learning Theories: Its Application to Effective Design of Collaborative Learning, \*S. Isotani and R. Mizoguchi: The Fifth International Workshop on Ontologies and Semantic Web for E-Learning (SWEL'07), Marina del Rey, CA, USA, July 9, 2007.

Standard-compliant Scenario Building with Theoretical Justification in a Theory-aware Authoring Tool (poster), \*Y. Hayashi, J. Bourdeau and R. Mizoguchi: The 13th International Conference on Artificial Intelligence in Education (AIED 2007), Marina del Rey, CA, USA, July 9-13, 2007.

Using Ontologies for an Effective Design of Collaborative Learning Activities (poster), \*S. Isotani and R. Mizoguchi: The 13th International Conference on Artificial Intelligence in Education (AIED 2007), Marina del Rey, CA, USA, July 9-13, 2007.

Deployment of Ontologies for an Effective Design of Collaborative Learning Scenarios, \*S. Isotani and R. Mizoguchi: 13th International Workshop on Groupware (CRIWG2007), Bariloche, Argentina, Sep. 16-20, 2007.

When the Domain of the Ontology is Education, \*J. Bourdeau, R. Mizoguchi, Y. Hayashi, V. Psyche and R. Nkambou: The 4th Conf. on Intelligent, Interactive Learning Objects Repository Networks (I2LOR'07), Montreal, Canada, Nov. 4-7, 2007.

Towards a Complete Ontology-aware Authoring Tool for Collaborative Learning, \*S. Isotani and R. Mizoguchi: The 15th International Conference on Computers in Education (ICCE2007), Hiroshima, Japan, Nov. 5-9, 2007.

Theory-aware Explanation Support for Standard-compliant Scenario Building, \*Y. Hayashi, J. Bourdeau and R. Mizoguchi: The workshop on Semantic Technology for Learning, Hiroshima, Japan, Nov. 5, 2007.

OOPS: User Modeling Method toward Realization of Task Oriented Mobile Internet Service Navigation (poster), \*M. Sasajima, Y. Kitamura, T. Naganuma, S. Kurakake and R. Mizoguchi: The 6th International Semantic Web Conference (ISWC2007), Busan, Korea, Nov. 11-15, 2007.

OOPS: User Modeling Method for Task Oriented Mobile Internet Services, \*M. Sasajima, Y. Kitamura, T. Naganuma, S. Kurakake and R. Mizoguchi: The 2007 IEEE/WIC/ACM International Conference on Web Intelligence 2007 (WI '07), Silicon Valley, USA, Nov. 2-5, 2007.

#### **Contributions to International Conferences and Journals**

|              |                                                                                                                                                                                                          |
|--------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| R. Mizoguchi | Semantic Web Science Association (Vice-president)                                                                                                                                                        |
| R. Mizoguchi | International Artificial Intelligence in Education Society (Executive Committee)                                                                                                                         |
| R. Mizoguchi | Asia-Pacific Society for Computers in Education (APSCE) (Board member)                                                                                                                                   |
| R. Mizoguchi | The 15 <sup>th</sup> International Conference on Computers in Education (ICCE2007) (PC member)                                                                                                           |
| R. Mizoguchi | The 12 <sup>th</sup> Conference of the Spanish Association for Artificial Intelligence and The Workshop on Artificial Intelligence Technology Transfer (CAEPIA - TTIA '07) (Scientific Committee member) |
| R. Mizoguchi | The 2 <sup>nd</sup> European Conference on Technology Enhanced Learning (EC-TEL 2007) (PC member)                                                                                                        |
| R. Mizoguchi | The 13 <sup>th</sup> International Conference on Artificial Intelligence in Education (AIED2007) (PC member)                                                                                             |
| R. Mizoguchi | The 4 <sup>th</sup> European Semantic Web Conference (ESWC2007) (PC member)                                                                                                                              |
| R. Mizoguchi | The 7 <sup>th</sup> IEEE International Conference on Advanced Learning Technologies (ICALT'07) (PC member)                                                                                               |
| R. Mizoguchi | The 2007 IEEE International Conference on Information Reuse and Integration (IEEE IRI-07) (PC member)                                                                                                    |

|              |                                                                                                                                             |
|--------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| R. Mizoguchi | The 16 <sup>th</sup> International World Wide Web Conference Semantic Web Track (PC Chair)                                                  |
| R. Mizoguchi | The 4 <sup>th</sup> International Conference on Knowledge Capture (K-CAP 2007) (PC member)                                                  |
| R. Mizoguchi | The 6 <sup>th</sup> international semantic web conference (ISWC2007) (General Chair)                                                        |
| R. Mizoguchi | The 5 <sup>th</sup> International Workshop on Applications of Semantic Web Technologies for E-Learning (SWEL'07) (Workshop Organizers)      |
| R. Mizoguchi | Workshop on Semantic Technology for Learning (PC member)                                                                                    |
| R. Mizoguchi | International Journal of Advanced Engineering Informatics (Editorial board)                                                                 |
| R. Mizoguchi | International Journal of Applied Ontology (Editorial board)                                                                                 |
| R. Mizoguchi | Research and Practice in Technology Enhanced Learning (Editorial board)                                                                     |
| R. Mizoguchi | International Journal of Artificial Intelligence in Education (Editorial board)                                                             |
| R. Mizoguchi | Frontiers in AI and Application (Editorial board)                                                                                           |
| R. Mizoguchi | International Journal of Web Engineering and Technology (Editorial board)                                                                   |
| R. Mizoguchi | International Journal of Web Semantics (Editorial board)                                                                                    |
| R. Mizoguchi | Journal of Educational Technology & Society (Editorial board)                                                                               |
| R. Mizoguchi | The 2 <sup>nd</sup> Asian Semantic Web Conference (Steering committee member)                                                               |
| Y. Kitamura  | The 6 <sup>th</sup> international semantic web conference (ISWC2007) (PC member)                                                            |
| Y. Kitamura  | The First International Workshop on Semantic Web and Web 2.0 in Architectural, Product and Engineering Design (Organizing Committee member) |
| Y. Hayashi   | The 5 <sup>th</sup> International Workshop on Applications of Semantic Web Technologies for E-Learning (SWEL'07) (PC member)                |
| Y. Hayashi   | The 14 <sup>th</sup> International Conference on Computers in Education (ICCE2007) (PC member)                                              |
| Y. Hayashi   | Workshop on Semantic Technology for Learning (PC member)                                                                                    |
| M. Sasajima  | The 4 <sup>th</sup> International Conference on Autonomic and Autonomous Systems (ICAS 2008) (PC member)                                    |

#### **Publications in Domestic Meetings**

|                                                                       |           |
|-----------------------------------------------------------------------|-----------|
| Japanese Society for Artificial Intelligence                          | 12 papers |
| The institute of Electronics, information and communication engineers | 1 paper   |
| Information Processing Society of Japan                               | 1 paper   |
| Japanese Society for Information and Systems in Education             | 1 paper   |

#### **Academic Degrees**

**Master Degree in Engineering**

|           |                                                                                      |  |
|-----------|--------------------------------------------------------------------------------------|--|
| M. Ookubo | A reference ontology-based mapping between functional taxonomies and its application |  |
|-----------|--------------------------------------------------------------------------------------|--|

**Sponsorship****Grant-in-Aid for Scientific Research on Priority Areas**

|              |                                                               |            |
|--------------|---------------------------------------------------------------|------------|
| R. Mizoguchi | Technical documents integration based on an artifact ontology | ¥5,200,000 |
|--------------|---------------------------------------------------------------|------------|

**Grant-in-Aid for Scientific Research (A)**

|              |                                                                 |             |
|--------------|-----------------------------------------------------------------|-------------|
| R. Mizoguchi | Building a Theory-aware and Standard-compliant Knowledge Server | ¥10,400,000 |
|--------------|-----------------------------------------------------------------|-------------|

**Grant-in-Aid for Young Scientists (B)**

|             |                                                                                          |            |
|-------------|------------------------------------------------------------------------------------------|------------|
| M. Sasajima | Research on modeling users' daily activities for improvement of mobile internet services | ¥1,100,000 |
|-------------|------------------------------------------------------------------------------------------|------------|

**Entrusted Research**

|              |                         |                                                                                                                                |             |
|--------------|-------------------------|--------------------------------------------------------------------------------------------------------------------------------|-------------|
| R. Mizoguchi | The University of Tokyo | Research on development of a medical knowledge database for medical information systems; Design of a semantic relational model | ¥10,000,000 |
|--------------|-------------------------|--------------------------------------------------------------------------------------------------------------------------------|-------------|

**Donation**

|              |                                 |            |
|--------------|---------------------------------|------------|
| R. Mizoguchi | Justsystem Corporation          | ¥5,000,000 |
| R. Mizoguchi | Y.M.P-International Corporation | ¥650,000   |
| R. Mizoguchi | Y.M.P-International Corporation | ¥650,000   |
| R. Mizoguchi | Teledream, Ltd.                 | ¥500,000   |

**Cooperative Research**

|              |                          |                                                                                                                                        |             |
|--------------|--------------------------|----------------------------------------------------------------------------------------------------------------------------------------|-------------|
| R. Mizoguchi | NTT DoCoMo, Inc.         | Research on an ontology for users in mobile environment to understand the real world context                                           | ¥3,000,000  |
| R. Mizoguchi | Justsystem Corporation   | Information sharing for safety-first manufacturing based on the unification of ontological engineering and natural language processing | ¥20,000,000 |
| R. Mizoguchi | Idemitsu Kosan Co., Ltd. | Development of knowledge base systems for nano-materials                                                                               | ¥3,300,000  |
| R. Mizoguchi | TOYOTA Info Technology   | Research on ontological techniques for automobiles                                                                                     | ¥1,000,000  |

Center Co., Ltd.

## Department of Intelligent Media

|                         |                                                                                                                                                                 |
|-------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Professor:              | Yasushi YAGI                                                                                                                                                    |
| Associate Professor:    | Yasuhiro MUKAIGAWA                                                                                                                                              |
| Assistant Professor:    | Ryusuke SAGAWA, Yasushi MAKIHARA                                                                                                                                |
| Designated Researchers: | Wang JUNQIU, Md. Altab HOSSAIN,<br>Kazuaki KONDO, Chunsheng HUA,<br>Tomohiro MASHITA                                                                            |
| Graduate Students:      | Nobuya AOKI, Hai VU,<br>Ngo Thanh Trung, Hidetoshi MANNAMI,<br>Takuro SAKAI, Kazuya SUZUKI,<br>Kazushige SUGIURA, Haruka AZUMA,<br>Kiyotaka AKASAKA, Akira TUJI |
| Undergraduates:         | Seiichi TAGAWA, Da Tan NGUYEN,<br>Nozomu TAJIRI, Shinji MURANAKA                                                                                                |
| Support Staff:          | Masako KAMURA, Noriko YASUI,<br>Yuko NAKAZAWA, Makiko FUJIMOTO                                                                                                  |

## Outlines

The studies in this laboratory focus on computer vision and media processing including basic technologies such as sensor design and camera calibration, and applications such as an intelligent system with visual processing functions. Some of our major research projects are development of a novel vision sensor, including an omnidirectional mirror, calibration of an omnidirectional vision system, video analysis for endoscopic diagnosis assistance, measurement of detailed reflectance properties, gait identification, modeling of environments.

## Current Research Project

### 1. Analysis of Subsurface Scattering under Generic Illumination

A scattering effect of incident lights called subsurface scattering occurs under the surface of translucent objects. In this paper, we present a method to analyze subsurface scattering from one image taken under generic illumination. In our method, diffuse subsurface reflectance in the subsurface scattering model can be linearly solved by quantizing the distances between each pair of surface patches. Then, the dipole approximation model is fit to the diffuse subsurface reflectance. By applying our method to real images, parameters of subsurface scattering can be computed from incident radiance, outgoing radiance, and 3-D geometry.

### 2. Omnidirectional Vision Attachment for Medical Endoscope

Medical endoscopes equips wide-angle lenses to provide wide fields of view for the convenience of medical doctors. However, it is pointed out that the backward of an endoscope becomes blind and an affected area is overlooked in the worst case, since the inside of the gastrointestinal system has a intricate shape by the plicae. In this paper, we propose an omnidirectional vision attachment that has a convex mirror and is equipped



at the tip of an endoscope. The attachment enables us to observe the backward of the endoscope with 360 degrees view. The issue to develop this attachment is the illumination of the field of view. Because the light source is only the light equipped at the tip of the endoscope when it is inside of the organ, we designed the attachment to illuminate the backward viewing field by reflecting the light by a mirror. In the experiment, we measured the field of view and the illuminated field, and validated that the backward of an endoscope can be observed by the attachment.

## **2. An Alignment Method of Small Compound Omnidirectional Sensor**

In this thesis, we propose an alignment method for a small and lightweight compound omnidirectional sensor which The small compound omnidirectional sensor consists of a convex hyperboloid mirror, a concave parabolic mirror, four convex parabolic mirrors and a camera. In this method , we first adjust the camera to the focus of convex hyperboloid mirror in order for the image to be correctly converted to the perspective projection image. Secondly, we adjust the camera to the focus of the concave parabolic mirror by using the optical characteristic that rays parallel to the axis of the mirror reflect toward its focus. Finally we set the four convex parabolic mirrors to the focus of the camera ,parallel to the axis of the concave parabolic mirror. The proposed method correctly aligns each mirror and the camera for the compound omnidirectional sensor, and , as a result we can detect near objects by azimuth difference between the mirrors and also obtain converted perspective projection image. Here we are presenting the effectiveness and the problems verified by the experiments of this alignment method.

## **3. Fast Measurement of Bidirectional Reflectance Distribution Function by Multiplexed Illumination**

For rapid measurement of BRDFs which express characteristics of reflection, many hardwares have been devised which exclude mechanical drives. In this paper, we introduce a new method to reduce the number of measurements of BRDF by composing multiple illumination. Multiple light sources, instead of a single light source, simultaneously illuminate the target object. We solve the overlapping problem of reflection by decomposing reflection into diffuse and specular components based on the dichromatic reflection model. We confirmed that the measuring time can be reduced by 8 times for measuring BRDF of a glossy coins.

## **Publications**

### **Original Papers**

Gait Identification Using a View Transformation Model in a Frequency Domain, Yasushi Makihara, Ryusuke Sagawa, Yasuhiro Mukaigawa, Tomio Echigo, Yasushi Yagi: IPSJ Transactions on Computer Vision and Image Media, 48 (SIG1(CVIM17)) (2007) 78-87.

Mirror Localization of Catadioptric Imaging System Using Parallel Lights, Nobuya Aoki, Ryusuke Sagawa, Yasuhiro Mukaigawa, Tomio Echigo, Yagi Yasushi: IPSJ Transactions on Computer Vision and Image Media, 49 (SIG9(CVIM18)) (2007) 115-123.

Anisotropic Omnidirectional Imaging System for Remote Surveillance of Devastated Area, Kasuaki Kondo, Yasuhiro Mukaigawa, Toshiya Suzuki, Yasushi Yagi: Transactions of the Virtual Reality Society of Japan, 12 (2) (2007) 137-148.

High Speed Measurement of BRDF using an Ellipsoidal Mirror, Kohei Sumino, Yasuhiro Mukaigawa, Yasushi Yagi: IEICE Transactions on Information and Systems, J90-D (8) (2007) 1930-1937.

A Probabilistic Method for Aligning and Merging Range Images with Anisotropic Error Distribution, Nanaho Osawa, Ryusuke Sagawa, Yasushi Yagi: IEICE Transactions on Information and Systems, J90-D (8) (2007) 1868-1877.

Adaptive Dynamic Range Camera with Reflective Liquid Crystal, Hidetoshi Mannami, Ryusuke Sagawa, Yasuhiro Mukaigawa, Tomio Echigo, Yasuhiro Yagi: IEICE Transactions on Information and Systems, J90-D (8) (2007) 1921-1929.

Adaptive Displaying Deformable Dissection Image of Intestine by Changing Point of Interest, Takurou Sakai, Suchit Pongnumkul, Ryusuke Sagawa, Tomio Echigo, Yasushi Yagi: IEICE Transactions on Information and Systems, J90-D (8) (2007) 2253-2261.

Accurate Calibration of Intrinsic Camera Parameters by Observing Parallel Light Pairs, Ryusuke Sagawa, Yasushi Yagi: IPSJ Transactions on Computer Vision and Image Media, 49 (SIG6(CVIM20)) (2008) 89-100.

A diagnosis support system for capsule endoscopy, Y. Yagi, H. Vu, T. Echigo, R. Sagawa, K. Yagi, M. Shiba, K. Higuchi, T. Arakawa: Inflammopharmacology, 15 (2) (2007) 78-83.

Adaptive dynamic range camera with reflective liquid crystal, Hidetoshi Mannami, Ryusuke Sagawa, Yasuhiro Mukaigawa, Tomio Echigo, Yasushi Yagi: Journal of Visual Communication and Image Representation, 18 (5) (2007) 359-365.

The Great Buddha Project: Digitally Archiving, Restoring, and Analyzing Cultural Heritage Objects, K. Ikeuchi, T. Oishi, J. Takamatsu, R. Sagawa, A. Nakazawa, R. Kurazume, K. Nishino, M. Kamakura and Y. Okamoto: International Journal of Computer Vision, 75 (1) (2007) 189-208.

Integrating Color and Shape-texture Features for Adaptive Real-time Tracking, Junqiu Wang, Yasushi Yagi: IEEE Trans. On Image Processing, 17 (2) (2008) 235-240.

A Compensation Method of Inter-reflection for Pattern Projection onto a Non-planar Surface, Yasuhiro Mukaigawa, Takayuki Kakinuma, Yuichi Ohta: IPSJ Transactions on Computer Vision and Image Media, 48 (SIG1(CVIM17)) (2007) 98-106.

Analysis of photometric factors based on photometric linearization, Y.Mukaigawa, Y.Ishii, T.Shakunaga: Journal of the Optical Society of America A, 24 (10) (2007) 3326-3334.

### **International Conferences**

Mirror Localization for a Catadioptric Imaging System by Projecting Parallel Lights, Ryusuke Sagawa, Nobuya Aoki, Yasuhiro Mukaigawa, Tomio Echigo, Yasushi Yagi: IEEE International Conference on Robotics and Automation.

Robust and Real-time Rotation Estimation of Compound Omnidirectional Sensor, Trung Ngo Thanh, Hajime Nagahara, Ryusuke Sagawa, Yasuhiro Mukaigawa, Masahiko Yachida, Yasushi Yagi: IEEE International Conference on Robotics and Automation.

High-Speed Measurement of BRDF using an Ellipsoidal Mirror and a Projector, Y.Mukaigawa, K.Sumino, Y.Yagi: Proc. IEEE International Workshop on Projector-Camera Systems (PROCAMS2007).

Development of a Networked Robotic System for Disaster Mitigation -System Description of Multi-robot System and Report of Performance Tests-, Keiji Nagatani, Kazuya Yoshida, Kiyoshi Kiyokawa, Yasushi Yagi, Tadashi Adachi, Hiroaki Saitoh, Toshiya Suzuki, Osamu Takizawa: The 6th International Conference on Field and Service Robotics.

Deformable Registration of Textured Range Images by Using Texture and Shape Features, Ryusuke Sagawa, Nanaho Osawa, Yasushi Yagi: The 6th International Conference on 3-D Digital Imaging and Modeling.

A Sensor for Simultaneously Capturing Texture and Shape by Projecting Structured Infrared Light, Kiyotaka Akasaka, Ryusuke Sagawa, Yasushi Yagi: The 6th International Conference on 3-D Digital Imaging and Modeling.

Contraction Detection in Small Bowel from an Image Sequence of Wireless Capsule Endoscopy (poster), Hai Vu, Tomio Echigo, Ryusuke Sagawa, Keiko Yagi, Masatsugu Shiba, Kazuhide Higuchi, Tetsuo Arakawa, Yasushi Yagi: Medical Image Computing and Computer-Assisted Intervention (MICCAI 2007).

High Dynamic Range Camera using Reflective Liquid Crystal, Hidetoshi Mannami, Ryusuke Sagawa, Yasuhiro Mukaigawa, Tomio Echigo, Yasushi Yagi: IEEE International Conference on Computer Vision.

Mirror Localization for Catadioptric Imaging System by Observing Parallel Light Pairs (poster), Ryusuke Sagawa, Nobuya Aoki, Yasushi Yagi: 8th Asian Conference on Computer Vision.

Multiplexed Illumination for Measuring BRDF using an Ellipsoidal Mirror and a Projector, Y.Mukaigawa, K.Sumino, Y.Yagi: 8th Asian Conference on Computer Vision.

Synchronized Ego-motion Recovery of Two Face-to-face Cameras (poster), J.Cui, Y.Yagi, H.Zha, Y.Mukaigawa and K.Kondo: 8th Asian Conference on Computer Vision.

Gait Identification based on Multi-view Observations using Omnidirectional Camera

(poster), K. Sugiura, Y. Makihara, and Y. Yagi: 8th Asian Conf. on Computer Vision.

Discriminative Mean Shift Tracking with Auxiliary Particles (poster), Junqiu Wang, Yasushi Yagi: 8th Asian Conf. on Computer Vision.

Consecutive Tracking and Segmentation Using Adaptive Mean Shift and Graph Cuts, Junqiu Wang, Yasushi Yagi: 2007 IEEE International Conference on Robotics and Biomimetics.

### **Contributions to International Conferences and Journals**

|              |                                                                                                         |
|--------------|---------------------------------------------------------------------------------------------------------|
| Y. Yagi      | Asian Conference on Computer Vision 2007 (ACCV2007)<br>(Program Chair)                                  |
| Y. Yagi      | IEEE International Conference on Robotics and Automation<br>2007 (Associate Editor)                     |
| Y. Yagi      | International Conference on Smart homes and health Telmatics<br>2007 (Organizing Committee)             |
| Y. Yagi      | The Korea-Japan Joint Workshop on Frontiers of Computer<br>Vision 2007 (Program Comittee)               |
| Y. Yagi      | International Journal of Automation and Computing (Editor)                                              |
| Y. Yagi      | IEEE International Conference on Computer Vision (Program<br>Committee)                                 |
| Y. Yagi      | Bentham Science Publishers Ltd. (Editorial Board Member)                                                |
| Y. Yagi      | IEEE International Conference on Robotics and Biomimetics<br>2007 (Program Committee)                   |
| Y. Yagi      | ACCV2007 Workshop on Multi-dimensional and Multi-view<br>Image Processing (Program Committee)           |
| Y. Yagi      | IEEE Computer Society Conference on Computer Vision and<br>Pattern Recognition 2008 (Program Committee) |
| Y. Mukaigawa | IEEE International Conference on Computer Vision (Program<br>Committee)                                 |
| Y. Mukaigawa | The 19th International Conference on Pattern Recognition<br>(Technical Committee)                       |
| Y. Mukaigawa | 8th Asian Conference on Computer Vision (Area Chair)                                                    |
| R. Sagawa    | 8th Asian Conference on Computer Vision (Technical Staff)                                               |
| R. Sagawa    | The 6th International Conference on 3-D Digital Imaging and<br>Modeling (Program Committee)             |
| Y. Makihara  | 8th Asian Conference on Computer Vision (Technical Staff)                                               |

### **Publications in Domestic Meetings**

|                                                 |          |
|-------------------------------------------------|----------|
| Information Processing Society of Japan         | 13papers |
| Symposium on Sensing via Image Information      | 3 papers |
| The Society of Instrument and Control Engineers | 1 paper  |

### **Academic Degrees**

#### **Master Degree for Information Science**

|           |                                                              |
|-----------|--------------------------------------------------------------|
| K. Suzuki | Analysis of Subsurface Scattering under Generic Illumination |
| T. Sakai  | Omnidirectional Vision Attachment for Medical Endoscope      |

## Sponsorship

### Grant-in-Aid for Scientific Research (S)

|         |                                                     |             |
|---------|-----------------------------------------------------|-------------|
| Y. Yagi | Wearable Omnidirectional Stereo Surveillance System | ¥25,610,000 |
|---------|-----------------------------------------------------|-------------|

### Grant-in-Aid for Young Scientists (A)

|              |                                                                         |            |
|--------------|-------------------------------------------------------------------------|------------|
| Y. Mukaigawa | Full measurement of spatially varying BRDF and its advanced application | ¥4,420,000 |
|--------------|-------------------------------------------------------------------------|------------|

### Other Research Fund

|         |                                                                                                                   |                                                                                |             |
|---------|-------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|-------------|
| Y. Yagi | Japan Science and Technology Agency, Special Coordination Funds for Promoting Science and Technology              | New Entertainment System "Dive Into the Movie"                                 | ¥61,829,000 |
| Y. Yagi | Ministry of Internal Affairs and Communications, Strategic Information and Communications R&D Promotion Programme | Multimedia Information Search by Teleoperated Robot Network in a Disaster Site | ¥390,000    |

## **Department of Architecture for Intelligence**

Professor: Masayuki NUMAO  
Associate Professor: Satoshi KURIHARA  
Assistant Professor: Koichi MORIYAMA  
Specially Appointed Assistant Professor: Ken-ichi FUKUI  
Post Doctoral Fellows: Roberto LEGASPI  
Graduate Students: Kazushi NAKAMURA, Minoru KAWANO,  
Ryozo KIYOHARA, Nagayoshi YAMASHITA,  
Akihiro OHTA, Hidenori FUKUI, Seiichi HONDA,  
Naofumi YASUBA, Toshihito SUGIMOTO,  
Hiroshi TAMAKI, Toshiyuki NISHIKAWA,  
Kazuhiro SATO, Ryo NAGAOKA  
Under Graduate Students: Shogo AKASAKI, Akihiro KAKEDA  
Supporting Staff: Fumie NAKAO, Sumiko SUGITA

### **Outlines**

The main research objective is to explore basic technology for computer systems, which support human learning and understanding, beyond conventional artificial intelligence. We particularly focus on the process of human-computer interaction to discover and create architecture of intelligence for such systems. We try to produce highly original research with findings from cognitive science, psychology, education, and computer science. Principal issues addressed are as follows: 1. Constructive Adaptive User Interfaces, 2. Intelligent Tutoring System, and 3. Intelligent Ubiquitous Sensor-Networks.

### **Current Research Project**

#### **Constructive Adaptive User Interfaces**

This department is developing a computer with learning ability, for which it researches efficient learning algorithms, acquisition of background knowledge for learning, application to Intelligent Tutoring Systems. These are applied to adaptive user interfaces. The conventional adaptive user interfaces only select a good response out of some previously given ones. Although this helps to use interfaces, such as a navigation system, it is not sufficient to stimulate human intelligence or creativity. The department has developed a method to compose a new content adaptively. This technology enables automatic acquisition of human feelings, and automatic music composition system adapted to personality and emotion of its user.

#### **Intelligent Tutoring System**

To have an instructional plan guide the learning process is significant to various teaching styles and an important task in an ITS. Though various approaches have been used to tackle this task, the compelling need is for an ITS to improve on its own the plans established in a dynamic way. We hypothesize that the use of knowledge derived from student categories can significantly support the improvement of plans on the part

of the ITS. This means that category knowledge can become effectors of effective plans. We have conceived a Category-based Self-improving Planning Module (CSPM) for an ITS tutor agent that utilizes the knowledge learned from learner categories to support self-improvement. The learning framework of CSPM employs unsupervised machine learning and knowledge acquisition heuristics for learning from experience. We have experimented on the feasibility of CSPM using recorded teaching scenarios.

### **Intelligent Ubiquitous Sensor-Networks**

In recent years, progress in computer technology, the appearance of IPv6, the development of various radio technology including IEEE802.11, and the practical use of radio-tags like RFID have greatly activated studies of ubiquitous computing like sensor-networks. But, the purpose of many proposed ubiquitous systems is to present information of the virtual-world like the Internet to humans living in the real-world by using physical properties like monitors and loudspeakers, etc. On the other hand, our purpose is to construct a framework to enable flexible and real-time interaction between humans and the real-world. Keyword is resonance. Each human has his own natural frequency, which is a metaphor for personality or daily habitual behaviors. In the proposed framework, each human behavior reacts with the environment and the environment performs sensor-data mining and extracts each human's natural frequency. The real-world that we assume in this study is homes and offices, etc., where daily habitual behaviors of humans are easy to extract. So, we call the real-world “the environment.” The environment learns the daily habitual behaviors of each human, and performs the most suitable interaction to whoever should receive it. To embody this interaction framework, the environment must be an autonomous action entity, and it is necessary to construct this entity as a massively multi-agent system to enable management and control of various broadly dispersed sensors and physical properties for interaction and to enable real-time interaction with humans. To begin with, we have set up several interaction devices between humans and the environment as well as various kinds of many sensors.

## **Publications**

### **Original Papers**

Keyword extraction From the Web Using Link Analysis Based Structural Equivalence, Nagayoshi Yamashita, Masayuki Numao, Satoshi Kurihara: Information Technology Letters, 6 (2007) 145-148.

Acquisition of Sensor-Network Topology based on Multi-Agent Pheromonal Coordination, Hiroshi Tamaki, Ken-ichi Fukui, Masayuki Numao, Satoshi Kurihara: Information Technology Letters, 6 (2007) 153-156.

Global Performances and Structures of Multi-Agent System due to Agent Selection Strategies, Toshiharu Sugawara, Satoshi Kurihara, Shin-ya Sato, Kensuke Fukuda, Osamu Akashi, Toshio Hirotsu: The Institute of Electronics, Information and Communication Engineers (IEICE), Transactions on Information and Systems, J90-D (3) (2007) 847-886.

Agent Organization system for Multi-agent based Network Management, Atsushi Terauchi, Osamu Akashi, Mitsuru Maruyama, Toshiharu Sugawara, Kensuke Fukuda, Toshio Hirotsu, Satoshi Kurihara, Keiichi Koyanagi: Transactions of the Japanese Society for Artificial Intelligence, 22 (5) (2007) 482-492.

Performance Characteristics of Contract Net Protocol in Massively Multi-Agent Systems, Toshiharu Sugawara, Kensuke Fukuda, Toshio Hirotsu, Satoshi Kurihara: Information Technology Letters, 6 (2007) 165-168.

On the Relationship between Word Bursts in Document Streams and Clusters in Lexical Co-occurrence Networks, Shin-ya Sato, Kensuke Fukuda, Toshiharu Sugawara, Satoshi Kurihara: The Information Processing Society of Japan, Transactions on Databases (IPSJ-TOD), 48 (SIG 14) (2007) 69-81.

Server-Client Load Distribution Technique based on Degree of Network Topology and its Evaluation, Kensuke Fukuda, Shin-ya Sato, Kazuo Hirotsu, Satoshi Kurihara, Toshiharu Sugawara: Japan Society for Software Science and Technology, Computer Software, 24 (4) (2007) 78-87.

Emergent Intelligence on Network: A survey, Satoshi Kurihara and Takashi Ishikawa: International Transactions on Systems Science and Applications, 3 (1) (2007) 3-10.

Accelerating Technique of Java for Hand-held Devices and Its Evaluation, Katsuhide Takahashi, Ryoza Kiyohara: Journal of Information Processing Society of Japan, 48 (2) (2007) 667-678.

Data Expression for Embedded Software, Ryoza Kiyohara, Satoshi Mii, Shigenori Kino: Journal of Institute of Electronics, Information and Communication Engineers (IEICE), J90-D (6) (2007) 1375-1382.

### **International Conferences**

Modelling Affective-based Music Compositional Intelligence with the Aid of ANS Analyses, \*Toshihito Sugimoto, Roberto Legaspi, Akihiro Ota, Koichi Moriyama, Satoshi Kurihara, Masayuki Numao: 27th SGAI International Conference on Artificial Intelligence, UK, Dec 2007.

Brainwave Production Creates Music Automatically (poster), \*Toshihito Sugimoto, Roberto Legaspi, Takayuki Nishikawa, Koichi Moriyama, Satoshi Kurihara, Masayuki Numao: 11th SANKEN and 6th Nanotechnology Center and 1st MSTEC International Symposium, Japan, Feb 2008.

Extracting Human Behaviors with Infrared Sensor Network, \*Seiichi Honda, Ken-ichi Fukui, Koichi Moriyama, Satoshi Kurihara, Masayuki Numao: 4th International Conference on Networked Sensing Systems, Germany, Jun 2007.

Automatic Acquisition of Sensor-Network Topology Based on Pheromone Communication Model (poster), Hiroshi Tamaki, \*Ken-ichi Fukui, Koichi Moriyama,



Satoshi Kurihara, Masayuki Numao: 4th International Conference on Networked Sensing Systems, Germany, Jun 2007.

Acquisition of Sensor-Network Topology Based on Multi-Agent Pheromonal Coordination, \*Hiroshi Tamaki, Ken-ichi Fukui, Masayuki Numao, Satoshi Kurihara: Workshop on Heterogeneous Agent Systems and Complex Networks (held in conjunction with ECCS2007), Germany, Oct 2007.

An Effective Selection of Abstract Plans for Multi-Agent Systems, \*Toshiharu Sugawara, Satoshi Kurihara, Toshio Hirotsu, Kensuke Fukuda, Toshihiro Takada: 27th SGAI International Conference on Artificial Intelligence, UK, Dec 2007.

Generating extensional definitions of concepts from ostensive definitions by using Web, \*Shin-ya Sato, Kensuke Fukuda, Satoshi Kurihara, Toshio Hirotsu, Toshiharu Sugawara: 8th International Conference on Web Information Systems Engineering, France, Dec 2007.

Performance Variation Due to Interference Among a Large Number of Self-Interested Agents, \*Toshiharu Sugawara, Toshio Hirotsu, Satoshi Kurihara, Kensuke Fukuda: IEEE Congress on Evolutionary Computation, Singapore, Sep 2007.

Case-Based Approach to Selecting Abstract Plans in Multi-Agent Systems, \*Toshiharu Sugawara, Satoshi Kurihara, Toshio Hirotsu, Kensuke Fukuda, Toshihiro Takada: Workshop of the Seventh International Conference on Case-Based Reasoning, UK, Aug 2007.

Multi-agent Coordination Mechanism based on Indirect Interaction (invited), \*Satoshi Kurihara, Kensuke Fukuda, Shinya Sato, Toshiharu Sugawara: International Symposium on Frontiers in Networking with Applications, Canada, May 2007.

Conflict Estimation of Abstract Plans for Multi-Agent Systems, \*Toshiharu Sugawara, Satoshi Kurihara, Toshio Hirotsu, Kensuke Fukuda, Toshihiro Takada: 6th International Joint Conference on Autonomous Agents and Multiagent Systems, USA, May 2007.

Context-Aware Middleware for Mobile Phone Based on Operational Logs, \*Ryozo Kiyohara, Mitsuhiro Matsumoto, Satoshi Mii, Naoki Shimizu, Masayuki Numao, Satoshi Kurihara: IEEE International Conference on Consumer Electronics, USA, Jan 2008.

Obtaining the Topological Map of Sensor Network with Pheromone System (poster), \*Hiroshi Tamaki, Ken-ichi Fukui, Masayuki Numao, Satoshi Kurihara: 11th SANKEN and 6th Nanotechnology Center and 1st MSTEC Internatinal Symposium, Japan, Feb 2008.

Reinforcement Learning on a Futures Market Simulator, \*Koichi Moriyama, Mitsuhiro Matsumoto, Ken-ichi Fukui, Satoshi Kurihara, Masayuki Numao: 1st KES Symposium on Agent and Multi-Agent Systems - Technologies and Applications (KES-AMSTA),

Poland, May/Jun 2007.

Utility Based Q-learning to Maintain Cooperation in Prisoner's Dilemma Games,  
\*Koichi Moriyama: IEEE/WIC/ACM International Conference on Intelligent Agent  
Technology, USA, Nov 2007.

### **Contributions to International Conferences and Journals**

|            |                                                                                                                                                                         |
|------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| M. Numao   | New Generation Computing (Area Editor)                                                                                                                                  |
| M. Numao   | Sixth International Joint Conference on Autonomous Agents and Multi-Agent Systems (AAMAS07)(Program Committee)                                                          |
| M. Numao   | The 1 <sup>st</sup> KES Symposium on Agent and Multi-Agent Systems (KES-AMSTA 2007)(Program Committee)                                                                  |
| M. Numao   | The Ninth ACIS International Conference on Software Engineering, Artificial Intelligence, Networking, and Parallel/Distributed Computing (SNPD2008) (Program Committee) |
| S.Kurihara | IEEE 7th International Conference on Computer and Information Technology (CIT'07) (Program Committee)                                                                   |
| S.Kurihara | The 2007 IEEE International Symposium on Ubisafe Computing (UbiSafe-07) (Program Committee)                                                                             |
| S.Kurihara | Workshop on Heterogeneous Agent Systems and Complex Networks in European Conference on Complex Systems (ECCS'07) (Program Committee)                                    |
| S.Kurihara | The 2nd International Workshop on Ubiquitous Application & Security Service (UASS-07) (Program Committee)                                                               |
| S.Kurihara | IEEE International Workshop on Learning in Multi-Agent Systems (LMAS-07) (Program Committee)                                                                            |
| S.Kurihara | 5th International Workshop on Networked Sensing Systems (INSS2008) (Program Committee)                                                                                  |
| S.Kurihara | The Second International Workshop on Coordination and Control in Massively Multi-Agent Systems (CCMMS 2008) (Program Committee)                                         |
| S.Kurihara | The Tenth Pacific Rim International Conference on Artificial Intelligence (PRICAI-08) (Program Committee)                                                               |
| S.Kurihara | 2008 Winter Workshop on Economics with Heterogeneous Interacting Agents (WEHIA) (Program Committee)                                                                     |
| S.Kurihara | Autonomic and Trusted Computing (ATC-08) (Program Committee)                                                                                                            |
| S.Kurihara | IEEE/WIC/ACM International Conference on Intelligence Agent Technology (IAT'08) (Program Committee)                                                                     |
| S.Kurihara | IEEE 8th International Conference on Computer and Information Technology (CIT'08) (Program Committee)                                                                   |
| S.Kurihara | The Third Workshop on Emergent Intelligence on Networked Agents (WEIN'08) (Program Committee Chair)                                                                     |
| S.Kurihara | The 9 <sup>th</sup> International Workshop on Multi-Agent-Based Simulation (MABS'08) (Program Committee)                                                                |

|            |                                                                                                                  |
|------------|------------------------------------------------------------------------------------------------------------------|
| S.Kurihara | The First International Workshop on Contents Creation Activity Support by Networked Sensing (CCASNS) (Organizer) |
| K.Moriyama | The 12th Pacific-Asia Conference on Knowledge Discovery and Data Mining (PAKDD 2008) (Local Arrangement Member)  |

### **Publications in Domestic Meetings**

|                                                                   |           |
|-------------------------------------------------------------------|-----------|
| Japanese Society of Artificial Intelligence                       | 12 papers |
| Information Processing Society of Japan                           | 5 papers  |
| Institute of Electronics, Information and Communication Engineers | 4 papers  |
| Japanese Society for Software Science and Technology              | 2 papers  |
| The Electrochemical Society of Japan                              | 1 paper   |

### **Academic Degrees**

#### **Master Degree for Information Science**

|              |                                                                                                        |
|--------------|--------------------------------------------------------------------------------------------------------|
| A. Ohta      | Predicting Evaluated Value of Music using Collaborative Filtering for the Automatic Composition System |
| H. Fukui     | Visualization and Extraction of Information Transition based on File Network                           |
| S. Honda     | Real-time Reactive Planning under Asynchronous Multi-goal Environment                                  |
| M. Matsumoto | Operation Prediction System for Mobile Phone using Context Information                                 |
| N. Yasuba    | Combining Quick-response and Consider Type Route Search Method for Navigation System                   |

### **Sponsorship**

#### **Grant-in-Aid for Young Scientists (B)**

|             |                                                |          |
|-------------|------------------------------------------------|----------|
| K. Moriyama | Deriving Appropriate Utility in Agent Learning | ¥800,000 |
|-------------|------------------------------------------------|----------|

#### **Entrusted Research**

|          |                                               |                                                                 |             |
|----------|-----------------------------------------------|-----------------------------------------------------------------|-------------|
| M. Numao | Japanese Society for the Promotion of Science | Investigation of science trend in artificial intelligence field | ¥14,500,000 |
|----------|-----------------------------------------------|-----------------------------------------------------------------|-------------|

#### **Other Research Fund**

|             |                                                       |                                                                                               |            |
|-------------|-------------------------------------------------------|-----------------------------------------------------------------------------------------------|------------|
| S. Kurihara | Artificial Intelligence Research Promotion Foundation | Study of real-time re-active planning for active interaction between human and the real-world | ¥500,000   |
| S. Kurihara | Ministry of Internal Affairs                          | Study of inter-ubiquitous network information                                                 | ¥9,748,700 |

|             |                                          |                                    |            |
|-------------|------------------------------------------|------------------------------------|------------|
|             | and<br>Communication<br>s                | infrastructure                     |            |
| S. Kurihara | Sumitomo<br>Electric<br>Industries, ltd. | Study for multi agent<br>framework | ¥2,970,000 |

## Department of Advanced Reasoning

Professor: Takashi WASHIO  
Research Associate: Kouzou OHARA, Akihiro INOKUCHI  
Graduate Students: HADIYANTO, Viet Phuong NGUYEN, Kentaro KIDO,  
Hiroshi KUWAJIMA, Kiyoto TAKABAYASHI,  
Kenta FUKATA, Noriyuki OHNISHI  
Under Graduate Students: Ha Hong NGUYEN, Vinh Duy NGUYEN  
Supporting Staff: Hiroko OKADA

### Outlines

We, humans, can extract variety of knowledge from given data by the full use of our reasoning. However, such reasoning ability of humans is so limited that most of the massive and complex data acquired through computer network are wasted without any humans' inspection. To provide efficient remedies to this difficulty, our department studies novel reasoning approaches to extract knowledge from the massive and complex data by using computers. These techniques are named data mining and knowledge discovery. We also study the application of these techniques to variety of fields such as science, information network, quality/risk management, medicine, security, marketing and finance. In this year, we obtained significant outcomes in the research topics of knowledge discovery from massively high dimensional dynamics data, knowledge discovery from graph structured data and knowledge discovery from massively high dimensional similarity data.

### Current Research Project

#### **Knowledge discovery from extremely high dimensional dynamics data**

Measurement data consisting of massive variables (extremely high dimensional data), which represent many events simultaneously occurred, became available by the development of computer network, ubiquitous sensing and scientific measurement technologies. Examples are the sales data of a large scale shopping center under various conditions and the profile data of thousands of gene expressions in biological systems. Our department started a new research topic to discover temporal dynamics and variable relations from such data acquired from large scale and complex systems in the last year. In this year, we further investigated this topic and developed more advanced methods.

We proposed an approach to model dynamics embedded in a given time series data where the events in each group co-occur in an objective system. This method enabled to identify the regularity of event occurrences from extremely high dimensional time series data such as the rule to predict popular sales items in a shop upon the popular sales in the other shops at a certain past time in the shopping center.

#### **Knowledge discovery from graph structured data**

There have recently been many attempts on data mining but most of them are targeted

to data in the standard transaction format or the relational database format. It appears that there are no effective methods that allow us to mine a dataset that has a more complex structure. Noting that most of the knowledge and concepts we handle can be represented in a graph structure, we have been working for the knowledge discovery from graph-structured data from various perspectives over the last ten years. The task of finding frequently appearing subgraphs (subgraph isomorphism) is known to be computationally hard and this is a very difficult problem to solve. In this year, we worked on the following two novel studies to overcome the limitations of the state of the art.

1) Development basic principles to derive large scale and frequent substructure co-occurrences

The size of the frequently co-occurred sub-graph structures which can be derived in the current graph mining techniques is limited to the structures consisting of a few dozens of vertices. Under the aim to overcome this limitation, we analyzed the properties of graph spectra to characterize the graph structures. We could clarify the mechanism that the graph spectra reflect their underlying graph structures, and confirmed the high feasibility to efficiently derive the frequently co-occurred sub-graph structures having large scale.

2) Development of basic principle to derive frequent graph sequences

The conventional framework of the graph mining remains to derive the frequently co-occurred sub-graph structures shared by many data graphs. In this year, we extended our research scope to efficiently derive frequently co-occurred sequence patterns embedded in graph series data. Upon the extensive explorations, we are almost establishing a practical mining approach to derive frequent graph subsequences.

### **Knowledge discovery from large scale similarity data**

We started the development of methods to efficiently derive correlation coefficients among thousands of variables from a given extremely high dimensional data in the last year. As massive computation power is required to compute correlation coefficients among huge number of variables, the efficient algorithm of this computation is highly important for causal reasoning among variables. This approach, which estimates objective correlation coefficients from the other known correlation coefficients, enabled to compute large number of correlation coefficients far more efficiently than their direct computation by using the given data. In this year, we extended this framework to estimate Euclidean distances among objects based on the Euclidean distances with the group of the other objects, and established a novel approach to efficiently compute accurate Euclidean distances

## **Publications**

### **Original Papers**

A Classification Method Based on Subspace Clustering and Association Rules, T. Washio, K. Nakanishi and H. Motoda: New Generation Computing, 25 (2007) 235-245.

Learning Personal Preference from Viewer's Operations for Browsing and its

Application to Baseball Video Retrieval and Summarization, N. Babaguchi, K. Ohara and T. Ogura: IEEE transactions on Multimedia, 9 (5) (2007) 1016-1025.

DryadeParent, an Efficient and Robust Closed Attribute Tree Mining Algorithm, A. Termier, M.-C. Rousset, M. Sebag, K. Ohara, T. Washio and H. Motoda: IEEE transactions on Knowledge and Data Engineering, 20 (3) (2008) 300-320.

An OLAP System for Text Analytics, A. Inokuchi and K. Takeda: IPSJ Transaction on Databases, 48 (11) (2007) 58-68.

### **Review Papers**

Data Intensive Computing – Mo.1 Discrete Structure Mining –, T. Washio, Journal of the Japanese Society for Artificial Intelligence, 22 [2] (2007) 263-271.

Application of Data Mining and Graph Mining to Causality Modeling, T. Washio, Chemical Information and Computer Sciences The Chemical Society of Japan Bulletin, 25 [3] (2007) 76-80.

The Pacific Rim International Conference on Artificial Intelligence (PRICAI 2006), K. Ohara, Journal of the Japanese Society for Artificial Intelligence, 22 [3] (2007) 353-355.

### **Books**

Advanced Engineering Informatics, Vol.21, Special Issue: Applications eligible for data mining, Takashi Washio (Ed.), Elsevier (2007) 241-301.

New Frontiers in Artificial Intelligence, JSAI 2006 Conference and Workshops, Tokyo, Japan, June 2006, Revised Selected Papers, LNAI 4384, T. Washio, K. Satoh, H. Takeda, and A. Inokuchi (Eds.), Springer (2007).

New Frontiers in Artificial Intelligence, JSAI 2006 Conference and Workshops, Tokyo, Japan, June 2006, Revised Selected Papers, LNAI 4384, T. Washio, K. Satoh, H. Takeda, and A. Inokuchi (Eds.), S. Tsumoto and T. Washio, Springer (2007) 303-304.

New Frontiers in Artificial Intelligence, JSAI 2006 Conference and Workshops, Tokyo, Japan, June 2006, Revised Selected Papers, LNAI 4384, T. Washio, K. Satoh, H. Takeda, and A. Inokuchi (Eds.) T. Washio, Y. Shinnou, K. Yada, H. Motoda and T. Okada, Springer (2007) 305-316.

Advances in Knowledge Acquisition and Management, Pacific Rim Knowledge Acquisition Workshop, PKAW 2006, Revised Selected Papers, LNAI 4303, A. Hoffmann, B.H. Kang, D. Richards and S. Tsumoto (Eds.), K. Takabayashi, P. C. Nguyen, K. Ohara, H. Motoda and T. Washio, Springer (2007) 64-74.

New Frontiers in Artificial Intelligence, JSAI 2003 and JSAI 2004 Conferences and Workshops, LNAI 3609, A. Sakurai, K. Hashida and K. Nitta (Eds.), W. Geamsakul, T. Matsuda, T. Yoshida, K. Ohara, H. Motoda, T. Washio, H. Yokoi and K. Takabayashi,

Springer (2007) 5-28.

Computational Discovery of Scientific Knowledge, Introduction, Techniques and Applications in Environmental and Life Sciences, LNAI4660, S. Dzeroski and L. Todorovski (Eds.), T. Washio and H. Motoda, Springer (2007) 98-119.

Emerging Technologies in Knowledge Discovery and Data Mining, LNAI 4819, T. Washio, Z. H. Zhou, J. Z. Huang, X. Hu, J. Li, C. Xie, J. He, D. Zou, K. C. Li and M. M. Freire (Eds.), Springer (2007).

Post Proceedings of JSAI 2007 Conference and Workshops, Miyasaki, Japan, June, 2007: New Frontiers in Artificial Intelligence, LNAI4914, K. Satoh, A. Inokuchi, K. Nagao and T. Kawamura (Eds.), T. Washio and S. Tsumoto, Springer (2008) 245-246.

Mechanical Engineering Handbook, Design Engineering, the Japan Society of Mechanical Engineers (Ed.), T. Washio, the Japan Society of Mechanical Engineers (2007) 202-205.

#### **Patents**

Multidimensional Data Analysis Method, Multidimensional Data Analysis System, and Their Programs, A. Inokuchi, T. Washio, and K. Takabayashi: No.2007-301025

Frequent Pattern Sequence Mining System, A. Inokuchi and T. Washio: 2008-044602

#### **International Conferences**

DIGDAG, a first algorithm to mine closed frequent embedded sub-DAGs, \*A. Termier, Y. Tamada, K. Numata, S. Imoto, T. Washio and T. Higuchi: MLG Workshop 2007, Mining and Learning with Graphs.

Fast PSD Matrix Estimation by Column Reductions, \*H. Kuwajima and T. Wasiho: The International Workshop on Data-Mining and Statistical Science (DMSS2007).

Large PSD Matrix Estimation from Partial Elements, \*H. Kuwajima and T. Washio: The Seventh IEEE International Conference on Data Mining - Workshop on High Performance Computing.

A Method for Online Analytical Processing of Text Data, \*A. Inokuchi and K. Takeda: The Sixteenth ACM Conference on Information and Knowledge Management.

Regression with Intervals, \*H. Kashima, K. Yamasaki, H. Saigo and A. Inokuchi: The International Workshop on Data-Mining and Statistical Science (DMSS2007).

#### **Contributions to International Conferences and Journals**

T. Washio                      The 11th Pacific-Asia Conference on Knowledge Discovery and Data Mining (PAKDD2007) (Workshop Chair)



|           |                                                                                                                                                    |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------|
| T. Washio | The 12th Pacific-Asia Conference on Knowledge Discovery and Data Mining (PAKDD2008) (Program Committee)                                            |
| T. Washio | Risk Mining Workshop 2007 (RM2007) (Program Chair)                                                                                                 |
| T. Washio | The 2007 IEEE Congress on Evolutionary Computation (CEC2007) (Program Committee)                                                                   |
| T. Washio | New Frontiers in Artificial Intelligence: Proceeding of the 19th Annual Conferences of the Japanese Society for Artificial Intelligence (Editor)   |
| T. Washio | International Conference on Mining and Learning with Graphs (Steering Committee)                                                                   |
| T. Washio | IADIS European First International Conference on Data Mining (Program Committee)                                                                   |
| T. Washio | The 10th International Conference on Discovery Science (DS2007) (Program Committee)                                                                |
| T. Washio | International Conference on Large-scale Knowledge Resources (ILKR2008) (Program Committee)                                                         |
| T. Washio | The 24th International Conference on Machine Learning (ICML2007) (Program Committee)                                                               |
| T. Washio | The 20th International Conference on Industrial, Engineering & Other Applications of Applied Intelligent Systems (IEA/AIE2007) (Program Committee) |
| T. Washio | The 6th European Conference on Computational Biology (ECCB) (Program Committee)                                                                    |
| T. Washio | The 15th Annual International Conference on Intelligent Systems for Molecular Biology (ISMB) (Program Committee)                                   |
| T. Washio | The 18th European Conference on Machine Learning (ECML) (Program Committee)                                                                        |
| T. Washio | The 11th European Conference on Principles and Practice of Knowledge Discovery in Databases (PKDD2007) (Program Committee)                         |
| T. Washio | The 24th International Conference on Mining and Learning 2007 Workshop on the Induction of Process Models(ICML2007) (Program Committee)            |
| T. Washio | The ACM 16th Conference on Information and Knowledge Management (CIKM2007) (Program Committee)                                                     |
| T. Washio | Data Mining and Knowledge Discovery (Editor)                                                                                                       |
| T. Washio | International Workshop on Constraint-Based Mining and Learning (Program Committee)                                                                 |
| T. Washio | Mining Graphs and Complex Structures (CGM'07), Workshop of ICDM2007: IEEE International Conference on Data Mining (Program Committee)              |
| T. Washio | International Workshop on Knowledge Discovery from Ubiquitous Data Streams (Program Committee)                                                     |
| T. Washio | The 8th SIAM International Conference on Data Mining (SDM) (Program Committee)                                                                     |

|             |                                                                                                                                                  |
|-------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| T. Washio   | The Fourteenth ACM SIGKDD International Conference on Knowledge Discovery and Data Mining (KDD-2008) (Program Committee)                         |
| T. Washio   | 2008 IEEE/WIC/ACM International Conference on Web Intelligence (WI'08) (Program Committee)                                                       |
| T. Washio   | The Eleventh International Conference on Discovery Science (DS-2008) (Program Committee)                                                         |
| T. Washio   | Algorithms for Large-Scale Information Processing in Knowledge Discovery (ALSIP 2008) (Program Committee)                                        |
| T. Washio   | ACM 17th Conference on Information and Knowledge Management (Program Committee)                                                                  |
| T. Washio   | The 10th Pacific Rim International Conference on Artificial Intelligence (PRICAI-08) (Program Committee)                                         |
| T. Washio   | The 2nd International Conference on Mining and Learning with Graphs (MLG-08) (Program Committee)                                                 |
| T. Washio   | The 10th Pacific Rim International Conference on Artificial Intelligence (PRICAI-08) (Workshop Chair)                                            |
| K. Ohara    | The 12th Pacific-Asia Conference on Knowledge Discovery and Data Mining (PAKDD2008) (Local arrangement Committee Co-Chair)                       |
| K. Ohara    | The 12th Pacific-Asia Conference on Knowledge Discovery and Data Mining (PAKDD2008) (Program Committee)                                          |
| K. Ohara    | The 17th Annual International Conference on Inductive Logic Programming (ILP2007) (Program Committee)                                            |
| K. Ohara    | The 2008 International Symposium on Ubiquitous Multimedia Computing (UMC2008) (Program Committee)                                                |
| A. Inokuchi | The 5th International Workshop on Mining and Learning with Graphs (MLG2007) (Program Committee)                                                  |
| A. Inokuchi | IADIS European First International Conference on Data Mining (ECDM2007) (Program Committee)                                                      |
| A. Inokuchi | The 12th Pacific-Asia Conference on Knowledge Discovery and Data Mining (PAKDD2008) (Publication Chair)                                          |
| A. Inokuchi | The 2nd International Workshop on Data-Mining and Statistical Science (DMSS2007) (Program Committee)                                             |
| A. Inokuchi | New Frontiers in Artificial Intelligence: Proceeding of the 20th Annual Conferences of the Japanese Society for Artificial Intelligence (Editor) |
| A. Inokuchi | The 12th Pacific-Asia Conference on Knowledge Discovery and Data Mining (PAKDD2008) (Program Committee)                                          |
| A. Inokuchi | IADIS European Second International Conference on Data Mining (ECDM2008) (Program Committee)                                                     |

#### **Publications in Domestic Meetings**

|                                              |           |
|----------------------------------------------|-----------|
| Japanese Society for Artificial Intelligence | 12 papers |
| Japan Statistical Society                    | 1 paper   |

## Academic Degrees

### Master Degree for Engineering

|                |                                                                            |  |
|----------------|----------------------------------------------------------------------------|--|
| K. Kido        | A Study on Fast and Accurate Euclidean Distance Estimation and Range Query |  |
| H. Kuwajima    | A Study on Fast PSD Estimation by Column Reduction                         |  |
| K. Takabayashi | A Study on Modeling Complex Sequential Data for OLAP Systems               |  |
| K. Fukata      | A Study on Retrieval Method of Identical Objects in Images                 |  |

## Sponsorships

### Grant-in Aid for Scientific Research(A)

|           |                                                                                                                                                |             |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| T. Washio | Development of Causal Structure Mining Method for Large Scale Dimensional Data and Construction of Knowledge Base on Gene Functional Relations | ¥15,730,000 |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------|-------------|

### Grant-in Aid for Scientific Research on Priority Area

|           |                                                                                                                                                     |            |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| T. Washio | Establishment of Knowledge Mining and Modeling Principles for Large Scale Dimensional Time Series and Its Application to Commercial Ubiquitous Data | ¥3,100,000 |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------|------------|

### Grant-in-Aid for Exploratory Research

|           |                                                                                                                              |          |
|-----------|------------------------------------------------------------------------------------------------------------------------------|----------|
| T. Washio | Development of Fast and Complete Search Method of Numeric Association Rules and Its Application to Medication Rule Discovery | ¥800,000 |
|-----------|------------------------------------------------------------------------------------------------------------------------------|----------|

### Grant-in-Aid for Young Scientists (B)

|          |                                                                          |            |
|----------|--------------------------------------------------------------------------|------------|
| K. Ohara | Development of Graph Mining Method Using Domain Knowledge as Constraints | ¥1,700,000 |
|----------|--------------------------------------------------------------------------|------------|

### Other Research Fund

|           |                                         |                                                                              |            |
|-----------|-----------------------------------------|------------------------------------------------------------------------------|------------|
| T. Washio | Daikin Industries, Ltd.                 | Exploration and Evaluation of Effective Approaches for Massive Data Analysis | ¥1,00,0000 |
| T. Washio | Toyota InfoTechnology Center, Co., Ltd. | A Study on Intelligent Information Processing for Car Industry               | ¥1,000,000 |
| T. Washio | AFOSR/AOAR D                            |                                                                              | ¥5,864,000 |

|           |                                                                                             |            |
|-----------|---------------------------------------------------------------------------------------------|------------|
| T. Washio | Kyoto                                                                                       | ¥1,800,000 |
| K. Ohara  | Technica, Inc.<br>The Ohkawa<br>Foundation for<br>Information and<br>Telecommunica<br>tions | ¥1,000,000 |

# Division of Biological Science

## Outline

The Division of Biological Sciences is composed of three departments: Dept. of Single-Molecule Biophysics, Dept. of Cell Membrane Biology, and Dept. of Structural Molecular Biology. These departments are engaged in researches in various fields of biological sciences including molecular enzymology, signal transduction, energy transformation, membrane transport, and mechanism of gene expression. The research projects covered by this division are as follows:

1. Single-molecule studies on the mechanochemical coupling of F- and V-type H<sup>+</sup> ATPases.
2. Single-molecule imaging of membrane proteins reconstituted in an artificial planar bilayer.
3. Developments of novel microdevices for highly sensitive detection of biological reactions.
4. The molecular structures and the molecular mechanisms of xenobiotic extruding pumps functioning as a host-defense mechanism in cellular level
5. Comprehensive studies on bacterial xenobiotic exporter genes and the regulation of the expression by two-component signal transduction systems
6. Physiological roles of efflux transporters in signal transduction and mammalian development
7. The mechanisms of biogenesis of the topa quinone cofactor in copper amine oxidase and other novel “built-in” cofactors in quinoxinoproteins
8. Identification of novel protein kinase C-interacting proteins and elucidation of their roles in signal transduction
9. Development of a new method of the gene delivery system using hepatitis B virus surface antigen particles

## Achievement

- Further insight into the mechanism of stereoselective proton abstraction by bacterial copper amine oxidase
- Involvement of MAPK signaling molecules and Runx2 in the NELL1-induced osteoblastic differentiation
- Development of a new bio-nanocapsule conjugated with liposome and its application for in vivo pinpoint delivery of various materials
- Development of femtoliter chamber made of water-in-oil emulsion
- Development of fluorescent protein sensor for live-cell ATP imaging
- Kinetic analysis of COPII vesicle by single molecule imaging
- Regulatory mechanism of the epsilon subunit of ATP synthase
- Study on the correlation between crystal structure of F1 and substeps of F1 found in the single-molecule rotation assay
- Development of a high-speed laser dark-field microscopy for 105 frame/sec imaging

- Studies on regulatory networks of xenobiotic exporters in *Salmonella enterica*
- Characterization of the lipophilic signal transducing molecules export system in the mammalian cells.
- Identification of the membrane exporter that mediates secretion of sphingosine-1-phosphate

## Department of Structural Molecular Biology

|                                          |                                                                                                                                                                                                                                                                |
|------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Professor:                               | Katsuyuki TANIZAWA                                                                                                                                                                                                                                             |
| Associate Professor:                     | Shun'ichi KURODA                                                                                                                                                                                                                                               |
| Assistant Professor:                     | Kenji TATEMATSU                                                                                                                                                                                                                                                |
| Specially Appointed Assistant Professor: | Takashi MATSUZAKI                                                                                                                                                                                                                                              |
| Post Doctoral Fellow:                    | Joo-Hee JUNG (2007.4.1-2007.9.30)                                                                                                                                                                                                                              |
| Part-time Researchers:                   | Nobuo YOSHIMOTO, Kazutoshi ONO<br>(2007.4.1-2008.1.31), Nobuyuki BOKUI<br>(2007.4.1-2008.2.29), Noriko SHIKAKU, Yoko<br>MATSUSHITA, Masumi IJIMA, Chizuko FUJITA                                                                                               |
| Visiting Research Scholar:               | Hana POSPISILOVA                                                                                                                                                                                                                                               |
| Graduate Students:                       | Takeshi, KASUYA, Mitsuo YAMADA, Hiroyuki TONOI,<br>Hiroshi SANPEI, Shota NAKANISHI, Atsushi NAGAMI,<br>Yasuo SASAKI, Mayumi NIIYAMA, Atsuro TADA,<br>Hidenori NONOMURA, Hiromichi YONEKURA, Akihito<br>MOTOYAMA, Yukari MATSUI, Yuko IKEDA, Noriko<br>NAKAGAWA |
| Supporting Staffs:                       | Mayuko MURAI, Ai OKUBO                                                                                                                                                                                                                                         |

### Outlines

The research of this laboratory is focused on the biochemical and molecular biological studies on various enzymes. Their active-site structures and catalytic mechanisms are being investigated by site-directed mutagenesis, various spectroscopies, and X-ray crystallography. A previous conspicuous finding is the copper ion-dependent, post-translational modification mechanism for the biogenesis of the topa quinone cofactor in copper amine oxidase. Furthermore, we investigate the intracellular mechanisms involving protein kinase C family, which play important roles in the cell proliferation, differentiation, oncogenesis, and apoptosis by cross talking with other molecules. Recently, we have succeeded to identify several protein kinase C-interacting proteins and characterized them as regulatory proteins for the protein kinase activities and/or their subcellular localization and also as effectors of kinase signaling. In addition, we have developed bio-nanocapsules displaying various biorecognition molecules, which are expected to be an ideal vector for the tissue- and cell type-specific gene and drug delivery system.

### Current Research Project

#### **Further Insight into the Mechanism of Stereoselective Proton Abstraction by Bacterial Copper Amine Oxidase**

During the catalytic reaction of copper amine oxidase, one of the two prochiral hydrogen atoms at the C1 position of substrate amine is stereoselectively abstracted by a conserved Asp residue serving as a general base. Using stereospecifically

deuterium-labeled enantiomers of 2-phenylethylamine, we previously showed that the *pro-S*  $\alpha$ -proton is abstracted by the enzyme from *Arthrobacter globiformis* (AGAO) [Uchida, M., et al. (2003) *Biosci. Biotechnol. Biochem.* 67, 2664–2667]. More recently, we have also demonstrated that the *pro-S* selectivity of  $\alpha$ -proton abstraction is fully retained even in the reaction of a mutant AGAO lacking the catalytic base [Chiu, Y.-C., et al. (2006) *Biochemistry* 45, 4105–4120]. Based on these findings, we have proposed that the stereoselectivity of  $\alpha$ -proton abstraction is primarily determined by the conformation of the Schiff-base intermediate formed between the substrate and the topa quinone cofactor (TPQ), stabilized by the binding of the distal part of the substrate to a hydrophobic pocket of the enzyme. In this conformation, the *pro-S* hydrogen atom to be abstracted is positioned nearly perpendicularly to the plane of the Schiff-base/TPQ conjugate system, achieving the maximum overlap of  $\sigma$  and  $\pi$  orbitals. To further elucidate the stereochemical details, we have synthesized stereospecifically deuterium-labeled enantiomers of ethylamine, a very poor substrate for AGAO, in addition to those structurally related to the preferred substrate, 2-phenylethylamine. In marked contrast to the nearly complete *pro-S* selectivity of  $\alpha$ -proton abstraction for most substrates examined, the stereoselectivity for ethylamine decreased significantly to as low as 88%. The crystal structure of AGAO soaked with ethylamine showed very poor electron densities for the substrate-Schiff base intermediate, showing that its conformation is not defined uniquely. Thus, the stereoselectivity of  $\alpha$ -proton abstraction during the copper amine oxidase reaction is closely associated with the conformational flexibility of the substrate-Schiff base intermediate.

### **Involvement of MAPK Signaling Molecules and Runx2 in the NELL1-induced Osteoblastic Differentiation**

NELL1 is an extracellular protein overexpressed in the sutures of craniosynostosis patients and has been identified as a novel osteogenic factor inducing osteogenic differentiation and bone formation of osteoblastic cells. To elucidate the intracellular signaling cascade evoked by NELL1 and leading to the bone formation, we have studied the direct effects of NELL1 protein on the cultured rat fetal calvarial cells using the recombinant human NELL1 (hNELL1) protein efficiently secreted by insect cells and purified to near homogeneity. We here show that hNELL1 protein induces the expression of several osteomarkers, such as alkaline phosphatase, osteopontin, and osteocalcin, and also transiently activates members of the MAPK signaling cascade including ERK, JNK, and p38. Particularly, the hNELL1-induced MAPK activation leads to the phosphorylation of Cbfa1, a central regulator of the bone formation, and expression of osteopontin. Unlike a well-known osteogenic factor BMP2, hNELL1 protein does not activate the Smad signaling cascade. Furthermore, hNELL1 protein has promoted the intracellular accumulation of Tyr-phosphorylated proteins within 2–5 min after the treatment. These findings suggest that upon binding to a specific receptor NELL1 transduces an osteogenic signal through activation of certain Tyr-kinases associated with the MAPK cascade, but not through the Smad cascade utilized in the BMP signal transduction, phosphorylates Cbfa1, and finally leads to the osteogenic differentiation.



## **Development of a New Bio-nanocapsule Conjugated with Liposome and Its Application for In Vivo Pinpoint Delivery of Various Materials**

Bio-nanocapsules (BNCs) consisting of hepatitis B virus (HBV) surface antigen (HBsAg) are approximately 50-nm hollow particles displaying a human hepatocyte-recognizing molecule (pre-S1 peptide). They have been used as an HB vaccine for the last two decades. Original BNC can incorporate various payloads (*e.g.*, drugs, genes) by electroporation and deliver them to human hepatocytes specifically by utilizing the HBV infection mechanism. Here, we developed a new BNC conjugated with liposome and succeeded in incorporating large materials (100-nm fluorescence-labeled polystyrene beads and >30 kbp plasmids) into the BNC-liposome complex. The complex delivered these large materials to human hepatocytes specifically *ex vivo* and *in vivo*. The transfection efficiency of the BNC-liposome complex was significantly higher than that of the original BNC. These results indicated that BNC confers the tissue- and cell-specificity on the conventional liposome and raises new possibilities for drug delivery systems, gene delivery systems, and bio-imaging systems *in vivo*.

## **Publications**

### **Original Papers**

Gene therapy of liver tumors with human liver-specific nanoparticles., Y. Iwasaki, M. Ueda, T. Yamada, A. Kondo, M. Seno, K. Tanizawa, S. Kuroda, M. Sakamoto, and M. Kitajima.: *Cancer Gene Ther.*, 14 (2007) 74-81.

Phosphorylation of Rho-associated kinase (Rho-kinase/ROCK/ROK) substrates by protein kinases A and C., J. H. Kang Y. Jiang, R. Toita, J. Oishi, K. Kawamura, A. Han, T. Mori, T. Niidome, M. Ishida, K. Tatematsu, K. Tanizawa, and Y. Katayama.: *Biochimie*, 89 (2007) 39-47.

Fasciculation and elongation protein zeta-1 (FEZ1) participates in the polarization of hippocampal neuron by controlling the mitochondrial motility., J. Ikuta, A. Maturana, T. Fujita, T. Okajima, K. Tatematsu, K. Tanizawa, and S. Kuroda.: *Biochem. Biophys. Res. Commun.*, 353 (2007) 127-132.

Characterization of bio-nanocapsule as a transfer vector targeting human hepatocyte carcinoma by disulfide linkage modification., T. Nagaoka, T. Fukuda, S. Yoshida, D. Yu, S. Kuroda, K. Tanizawa, A. Kondo, M. Ueda, H. Yamada, H. Tada, and M. Seno.: *J. Control. Release*, 118 (2007) 348-356.

Axonal guidance protein FEZ1 associates with tubulin and kinesin motor protein to transport mitochondria in neurites of NGF-stimulated PC12 cells., T. Fujita, A. D. Maturana, J. Ikuta, J. Hamada, S. Walchli, T. Suzuki, H. Sawa, M. W. Wooten, T. Okajima, K. Tatematsu, K. Tanizawa, and S. Kuroda.: *Biochem. Biophys. Res. Commun.*, 361 (2007) 605-610.

Trapping of a dopaquinone intermediate in the TPQ cofactor biogenesis in a copper-containing amine oxidase from *Arthrobacter globiformis*., R. H. Moore, M. A.

Spies, M. B. Culpepper, T. Murakawa, S. Hirota, T. Okajima, K. Tanizawa, and M. Mure.: *J. Am. Chem. Soc.*, 129 (2007) 11524-11534.

Involvement of MAPK signaling molecules and Runx2 in the NELL1-induced osteoblastic differentiation., N. Bokui, T. Otani, K. Igarashi, J. Kaku, M. Oda, T. Nagaoka, M. Seno, K. Tatematsu, T. Okajima, T. Matsuzaki, K. Ting, K. Tanizawa, and S. Kuroda.: *FEBS Lett.*, 582 (2008) 365-371.

Optimal surface chemistry for peptide immobilization in on-chip phosphorylation analysis., K. Inamori, M. Kyo, K. Matsukawa, Y. Inoue, T. Sonoda, K. Tatematsu, K. Tanizawa, T. Mori, and Y. Katayama.: *Anal. Chem.*, 80 (2008) 643-650.

Bio-nanocapsule conjugated with liposomes for in vivo pinpoint delivery of various materials., J. H. Jung, T. Matsuzaki, K. Tatematsu, T. Okajima, K. Tanizawa, and S. Kuroda: *J. Control. Release*, 126 (2008) 255-264.

A cold-active and thermostable alcohol dehydrogenase of a psychrotolerant from Antarctic seawater, *Flavobacterium frigidimaris* KUC-1., T. Kazuoka, T. Oikawa, I. Muraoka, S. Kuroda, and K. Soda.: *Extremophiles*, 11 (2007) 257-267.

Synergistic effects of Nell-1 and BMP-2 on the osteogenic differentiation of myoblasts., C. M. Cowan, X. Jiang, T. Hsu, C. Soo, B. Zhang, J. Z. Wang, S. Kuroda, B. Wu, Z. Zhang, X. Zhang, and K. Ting.: *J. Bone Miner. Res.*, 22 (2007) 918-930.

The MAP kinase p38 links Shiga toxin dependent signaling and trafficking., S. Wälchli, S. S. Skånland, T. F. Gregers, S.U. Lauvrak, M. L. Torgersen, M. Ying, S. Kuroda, A. Maturana, and K. Sandvig.: *Mol. Biol. Cell*, 19 (2008) 95-104.

## **Review Papers**

Development of bio-nano carrier and its application to cancer gene therapy, A. Kondo, S. Kuroda, K. Tanizawa, M. Seno, and M. Ueda: *Biotechnology Journal*, 7 (2007) 41-47.

Bio-nanocapsules for in vivo pinpoint drug delivery, J.-H. Jung, T. Kasuya, K. Tanizawa, and S. Kuroda: *Yakugaku Zasshi*, 127 (2007) 797-805.

## **Books**

“Nanoparticle Technology Handbook (Chapter 37: Pinpoint Drug and Gene Delivery)” (M. Hosokawa, K. Nogi, M. Naito, and T. Yokoyama, Eds.), S. Kuroda, Elsevier, Amsterdam, the Netherlands (2007)

“Comprehensive Nano-Bio Handbook (Drug delivery system: p. 360)” (T. Yamane, and T. Matsunaga, Eds.), T. Yamada and S. Kuroda, Techno System, Tokyo, Japan (2007)

“Comprehensive Nano-Bio Handbook (Bio-nanocapsule: pp. 313-315)” (T. Yamane, and T. Matsunaga, Eds.), T. Yamada and S. Kuroda, Techno System, Tokyo, Japan (2007)

“Comprehensive Nano-Bio Handbook (Virus: p. 77)” (T. Yamane, and T. Matsunaga, Eds.), T. Yamada and S. Kuroda, Techno System, Tokyo, Japan (2007)

“Comprehensive Nano-Bio Handbook (Pharmacogenomics: pp. 159-161)” (T. Yamane, and T. Matsunaga, Eds.), K. Tatemastu and S. Kuroda, Techno System, Tokyo, Japan (2007)

“Comprehensive Nano-Bio Handbook (Signal Transduction System: pp. 223-225)” (T. Yamane, and T. Matsunaga, Eds.), K. Tatemastu and S. Kuroda, Techno System, Tokyo, Japan (2007)

### **Patents**

“Carriers using Protein Hollow Nanoparticles” S. Kuroda, K. Tanizawa, M. Seno, A. Kondo, and M. Ueda: Registered Japan Patent 408531.

“Drugs using Protein Hollow Nanoparticles Fused with Therapeutic Proteins” S. Kuroda, K. Tanizawa, A. Kondo, M. Seno, and H. Tada: Registered Korean Patent 10-0686356.

“Model Animals Harboring Liver Cirrhosis” S. Kuroda, K. Tanizawa, A. Kondo, M. Seno, and M. Ueda: Registered Japan Patent 3964278.

“Model Animals Harboring Liver Cirrhosis” S. Kuroda, K. Tanizawa, A. Kondo, M. Seno, and M. Ueda: Registered Korean Patent 10-0676010.

“Drug Using Protein Hollow Nanoparticles” S. Kuroda, K. Tanizawa, A. Kondo, M. Ueda, and M. Seno: Registered Korean Patent 10-0674325.

“Biotinylated Nanoparticles for Immunological Assays” S. Hiramatsu, G.-M. Jung, S. Hatahira, D. Kanamori, H. Kadoya, S. Kuroda, and K. Tanizawa: JP 2007-3677.

“Complex Particles for Drug Delivery System” N. Shimizu, C. Ogino, and S. Kuroda: JP2007-032765.

“Screening Method of Agonist and Antagonist for Auto-phosphorylated Receptors and Genetically Recombinated Yeasts” K. Tatematsu, S. Kuroda, N. Yoshimoto, N. Shikaku, and K. Uemukai: JP2007-92492.

“Drugs and Medical Supplies Containing a Protein Having Bone and Cartilage Forming Activities” M. Nakamura, S. Kuoroda, J. Sumi, M. Oda, M. Matanihara, Y. Kenmochi, N. Bokui, and K. Igarashi: JP2007-286810.

“Bionanocapsules for Material Delivery and Bio-imaging Using Sugar and Sugar-chain Recognizing Mechanism” S. Kuroda, H. Miyoshi, and S. Hizume: JP2007-296127.

“Bionanocapsules for Material Delivery Specifically to Inflammatory Regions” S. Kuroda, Y. Tano, N. Daikoku, S. Hizume: JP2007-296136.

“Drug Delivery System” H. Aoki, K. Yoshimura, H. Tsutsumi, C. Teruyama, M. Matsuzaki, and S. Kuroda: JP2007-331948.

“Biotinylated Nanoparticles for Immunological Assays” S. Hiramatsu, G.-M. Jung, S. Hatahira, D. Kanamori, H. Kadoya, S. Kuroda, and K. Tanizawa: JP 2008-001124.

“Efficient Purification Method for Bionanocapsules” S. Kuroda, Y. Maekawa, and M. Nagita: PCT/JP2007/052414.

### **International Conferences**

Structural basis for stereospecific proton abstraction of bacterial copper amine oxidase. (poster), \*T. Okajima, T. Murakawa, Y.-C. Chiu, M. Taki, Y. Yamamoto, H. Hayashi, and K. Tanizawa: 2nd International Symposium on Diffraction Structural Biology 2007 (ISDSB2007), Tokyo, Japan, September 10-13, 2007.

A subtilisin-like protease essential for the biogenesis of quinoxinoprotein amine dehydrogenase (poster), \*T. Okajima, K. Ono, A. Nagami, M. Niiyama, and K. Tanizawa.: Gordon Research Conference on Protein Cofactors, Radicals and Quinones, Ventura, California, U.S.A., January 20-25, 2008.

Conformational flexibility of the TPQ cofactor in bacterial copper amine oxidase. (poster), \*T. Okajima, S. Nakanishi, T. Murakawa, H. Hayashi, and K. Tanizawa.: Gordon Research Conference on Protein Cofactors, Radicals and Quinones, Ventura, California, U.S.A., January 20-25, 2008.

Hydrogen tunneling in bacterial copper amine oxidase reaction (poster), \*T. Murakawa, T. Okajima, S. Nakanishi, H. Hayashi, and K. Tanizawa: Gordon Research Conference on Protein Cofactors, Radicals and Quinones, Ventura, California, U.S.A., January 20-25, 2008.

Bio-nanocapsule displaying homing peptide, a novel in vivo pinpoint gene and drug delivery system (poster), \*T. MATSUZAKI, H. TONOI, J.H. JUNG, K. TANIZAWA, and S. KURODA: 3rd Annual Meeting of The American Academy of Nanomedicine, University of California at San Diego, San Diego, CA, USA, September 7-9, 2007.

Analysis of HBV entry using yeast-derived HBsAg L particle: Role of putative HBV receptor SCCA1 (poster), \*T. KASUYA, J.H. JUNG, T. MATSUZAKI, M. YAMADA, K. TANIZAWA, and S. KURODA: International Meeting, The Molecular Biology of Hepatitis B Viruses, Roma, Italy, September 16-20, 2007.

Bio-nanocapsule displaying homing peptide, a novel in vivo pinpoint gene and drug delivery system (poster), \*T. MATSUZAKI, H. TONOI, J.H. JUNG, K. TANIZAWA, and S. KURODA: 11th Sanken International Symposium/6th Nanotechnology Center International Symposium/1st MSTE International Symposium, Awaji Yumebutai International Conference Center, Hyogo, Japan, February 4-5, 2008.

Analysis of HBV entry using yeast-derived HBsAg L particle: Role of putative HBV

receptor SCCA1 (poster), \*T. KASUYA, J.H. JUNG, T. MATSUZAKI, M. YAMADA, K. TANIZAWA, and S. KURODA: 11th Sanken International Symposium/6th Nanotechnology Center International Symposium/1st MSTEC International Symposium, Awaji Yumebutai International Conference Center, Hyogo, Japan, February 4-5, 2008.

Response regulator YycF essential for bacterial growth: X-ray crystal structure of the DNA-binding domain and its PhoB-like DNA recognition. (poster), \*A. Tada, T. Okajima, A. Doi, A. Okada, Y. Gotoh, R. Utsumi, and K. Tanizawa.: 11th Sanken International Symposium/6th Nanotechnology Center International Symposium/1st MSTEC International Symposium, Awaji Yumebutai International Conference Center, Hyogo, Japan, February 4-5, 2008.

Development of Ligand Screening System Specific for Cytokine Receptor (invited), \*S. Kuroda: International Bio EXPO 2007, Tokyo BigSight, June 22, 2007.

Bio-nanocapsule for In Vivo Pinpoint Drug and Gene Delivery System (invited), \*S. Kuroda: The 2nd Korea-Japan Workshop on Combinatorial Bioengineering, June 29, 2007, COEX, Seoul, Korea.

#### **Contributions to International Conferences and Journals**

|             |                                                                                               |
|-------------|-----------------------------------------------------------------------------------------------|
| K. Tanizawa | Federation of Asian and Oceanian Biochemists and Molecular Biologists (Delegate of Japan)     |
| K. Tanizawa | The Journal of Biochemistry (Associate Editor)                                                |
| K. Tanizawa | Journal of Nutritional Science and Vitaminology (Associate Editor)                            |
| S. Kuroda   | The Open Veterinary Science Journal, Bentham Science Publishers Ltd. (Editorial Board Member) |

#### **Publications in Domestic Meetings**

|                                                                                                               |           |
|---------------------------------------------------------------------------------------------------------------|-----------|
| Joint Annual Meeting of the Molecular Biology Society of Japan and the Japanese Biochemical Society (BMB2007) | 15 papers |
| Annual Meeting of the Japanese Biotechnology Society                                                          | 1 paper   |
| Annual Meeting of the Japanese DDS Society                                                                    | 5 papers  |

#### **Academic Degrees**

##### **Doctor Degree for Science**

|          |                                                                                         |
|----------|-----------------------------------------------------------------------------------------|
| N. Bokui | Intracellular Signal Cascade Involved in the NELL1-induced Osteoblastic Differentiation |
|----------|-----------------------------------------------------------------------------------------|

##### **Master Degree for Science**

|           |                                                                                           |
|-----------|-------------------------------------------------------------------------------------------|
| H. Sanpei | Re-targeting of Bionanocapsules Used for DDS by Surface-displaying Sugar Chains           |
| Y. Sasaki | Analysis of Membrane Fusion Activity of Hepatitis B Virus Envelope Protein Using Liposome |
| A. Nagami | Mechanism of Formation and Structural Role of Intramolecular                              |

|            |                                                                                                                                                   |
|------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| M. Niiyama | Thio-ether Crosslinks in Quinohemoprotein Amine Dehydrogenase<br>Mechanism of Quinone Cofactor Biogenesis in Quinohemoprotein Amine Dehydrogenase |
|------------|---------------------------------------------------------------------------------------------------------------------------------------------------|

### Master Degree for Engineering

|              |                                                                                  |
|--------------|----------------------------------------------------------------------------------|
| S. Nakanishi | Role of Conserved Asn Residue in the Catalytic Mechanism of Copper Amine Oxidase |
|--------------|----------------------------------------------------------------------------------|

### Sponsorship

#### Grant-in-Aid for Scientific Research on Priority Areas (C) (2)

|           |                                                                                                         |            |
|-----------|---------------------------------------------------------------------------------------------------------|------------|
| S. Kuroda | Development of Missile Therapy Using Hollow Bionanoparticles Displaying Cancer Specific Homing Peptides | ¥6,400,000 |
|-----------|---------------------------------------------------------------------------------------------------------|------------|

#### Grant-in-Aid for Scientific Research (B)

|             |                                                                            |            |
|-------------|----------------------------------------------------------------------------|------------|
| K. Tanizawa | Mechanisms of Biosynthesis and Catalysis of Built-in Type Quinone Cofactor | ¥3,380,000 |
|-------------|----------------------------------------------------------------------------|------------|

#### Health and Labour Sciences Research Grants

|           |                                                                                  |            |
|-----------|----------------------------------------------------------------------------------|------------|
| S. Kuroda | Development of Therapy for Acute Myocardial Infarction Using Nano-sized Liposome | ¥4,000,000 |
|-----------|----------------------------------------------------------------------------------|------------|

#### Entrusted Research

|             |                                                                  |                                                                                                                                                                                                                                 |              |
|-------------|------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|
| K. Tanizawa | Japan Science and Technology Agency (CREST)                      | Creation of Functional Materials/ System that Utilize Nano Biotechnology for Realizing a Noninvasive Medical Treatment System: Novel Cell-selective Gene Delivery System Using Intracellular Signal-responsive Molecular System | ¥7,540,000   |
| K. Tanizawa | Bio-oriented Technology Research Advancement Institution (BRAIN) | Development of Innovative and Hypersensitive Bio-sensing Technology Using Yeast-derived Bio-nanocapsule                                                                                                                         | ¥20,000,000  |
| S. Kuroda   | Japan Science and Technology Agency (Promotion Program of        | Development of Bio-nanoparticles for Pinpoint Drug Delivery System in Medical Field                                                                                                                                             | ¥115,000,000 |

Utilization of  
Regional  
Research and  
Development)

**Cooperative Research**

|           |                  |                                                              |            |
|-----------|------------------|--------------------------------------------------------------|------------|
| S. Kuroda | GenoLac BL Corp. | Production and Development of<br>New Live Bacterial Vaccines | ¥1,000,000 |
|-----------|------------------|--------------------------------------------------------------|------------|

**Other Research Fund**

|              |                             |            |
|--------------|-----------------------------|------------|
| K. Tanizawa  | Vitamin B Committee         | ¥250,000   |
| K. Tatematsu | Protein Research Foundation | ¥600,000   |
| K. Kuroda    | GenoLac BL Corp.            | ¥1,000,000 |

## Department of Single Molecule Biophysics

|                          |                                                                                                                                                          |
|--------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| Professor:               | Hiroyuki NOJI                                                                                                                                            |
| Associate Professor:     | Yoh WADA                                                                                                                                                 |
| Assistant Professors:    | Kazuhito TABATA, Ryota IINO                                                                                                                              |
| Post Doctoral Fellows:   | Daichi OKUNO, Hiromi IMAMURA, Hiroshi UENO, Liza LAM, Sawako ENOKI                                                                                       |
| Graduate Students:       | Junya HORIGUCHI, Masayoshi NAKATA, Ryo FUJISAWA, You HUIJUAN, Mizue TANIGAWARA, Yoshito KOMORIYA, Mariko NAKAMURA, Yoshihiro NISHIKAWA, Uner Nacite ESMA |
| Under Graduate Students: | Kumiko ARATA, Hiroko TOGAWA, Yuki MATSUKAGE                                                                                                              |
| Supporting Staffs:       | Rie HASEGAWA, Kunihiro YOSHIKAWA, Kohei HAYAMA,                                                                                                          |
| Secretaries:             | Lisa DATE, Machiko NAKANISHI                                                                                                                             |

### Outlines

Our main research objective is to reveal energy-conversion mechanism of biomolecular motors using single-molecule imaging and single-molecule manipulation techniques. Currently, we launched research projects of micro- and bio-devices to realize high sensitive and high throughput detection of biological reactions using micro/nano technology. We conduct quite interdisciplinary researches crossing biophysics, biochemistry, nanotechnology, and micro/nano fabrication.

### Current Research Project

#### 1. Single-molecule studies on a rotary molecular motor, $F_0F_1$ -ATP synthase

$F_1$ -ATPase is a rotary molecular motor that makes 120° stepping rotation, each step driven by a single ATP hydrolysis reaction. Recently, a new reaction intermediate of  $F_1$ -ATPase was discovered at 4°C, as an intervening pause at the same angle for pre-ATP-binding state.

#### 2. Imaging of COPII vesicle formation and budding from artificial membrane

COPII system is responsible for the vesicle formation from endoplasmic reticulum in eukaryotic cells. We have succeeded in the real time observation of the process of COPII vesicle formation in the reconstituted system, and are investigating the mechanism of substrate selection into the vesicle.

#### 3. Development of novel, FRET-based ATP sensor for living cells

By using the fluorescent proteins from *A. Victoria*, we are developing novel ATP sensor that can be used in living cells.

#### 4. Development of femtoliter droplet array

Femtoliter droplet chamber array was developed by utilizing the surface with amphiphilic properties, and single molecule enzymatic activity measurement was carried out.



## **Publications**

### **Original Papers**

Temperature-sensitive reaction intermediate of F1-ATPase., R. Watanabe, R. Iino, K. Shimabukuro, M. Yoshida, H. Noji: EMBO Reports, 9 (2008) 84-90.

Thermally responsive supramolecular nanomeshes for on/off switching of the rotary motion of F1-ATPase at the single-molecule level., S. Yamaguchi, S. Matsumoto, K. Ishizuka, Y. Iko, K.V. Tabata, H.F. Arata, H. Fujita, H. Noji, I. Hamachi: Chemistry, 14 (2008) 1891-1896.

An integrated system for enzymatic cleavage and electrostretching of freely-suspended single DNA molecules, L. Lam, S. Sakakihara, K. Ishizuka, S. Takeuchi, H. Noji: Lab on a Chip, 7 (2007) 1738-1745.

Lipid bilayer microarray for parallel recording of transmembrane ion currents, B. Pioufle, H. Suzuki, K.V. Tabata, H. Noji, S. Takeuchi.: Analytical Chemistry, 80 (2007) 328-332.

Coupling of rotation and catalysis in F(1)-ATPase revealed by single-molecule imaging and manipulation, K. Adachi, K. Oiwa, T. Nishizaka, S. Furuie, H. Noji, H. Itoh, M. Yoshida, K. Jr Kinosita: Cell, 130 (2007) 309-321.

Visualization of RecA filaments and DNA by fluorescence microscopy, T. Nishinaka, Y. Doi, M. Hashimoto, R. Hara, T. Shibata, Y. Harada, K. Jr Kinosita, H. Noji, E. Yashima.: Journal of Biochemistry, 141 (2007) 147-156.

Single molecule energetics of F1-ATPase motor, E. Muneyuki, T. Watanabe-Nakayama, T. Suzuki, M. Yoshida, T. Nishizaka, H. Noji.: Biophysical Journal, 92 (2007) 1806-1812.

GPI-anchored receptor clusters transiently recruit Lyn and G  $\alpha$  for temporary cluster immobilization and Lyn activation: Single-molecule tracking study 1, K.G.N Suzuki., TK. Fujiwara, F. Sanematsu, R. Iino, M. Edidin, A. Kusumi: Journal of Cell Biology, 177 (2007) 717-730.

### **Review Papers**

Highly-sensitive Restriction Enzyme Assay and Analysis: A Review. Lam, L., Iino, R., Tabata, K. V. and Noji H. Analytical and Bioanalytical Chemistry. In press.

### **International Conferences**

Single Molecule Studies on F1-ATPase (invited), H. Noji: International Symposium on Hierarchy and Holism (ISHH), "Bridging across Different Hierarchies in Natural Sciences", Okazaki, Japan, February 23, 2008.

Single Molecule Studies on F1-ATPase (invited), H. Noji: 3rd work shop of the

UK-Japan Bionanotechnology Collaboration, Oxford, UK, July 19, 2007.

Single Molecule Studies on F1-ATPase (plenary), H. Noji: Autumn School for PhD students and young researcher (NAMIS) 2007, Tokyo, Japan, November 5, 2007.

Single Molecule Studies on F1-ATPase (invited), H. Noji: The 6th JSPS Forum in France, "Chemical and physical nanobiology for medicine", Strasbourg, France, November 23, 2007.

Chemomechanical coupling of F1-ATPase motor protein (invited), H. Noji: SANKEN WORKSHOP on Nano-Bioscience at Berkeley, Berkeley, USA, March 21-22, 2007.

Highly sensitive measurement of biological reaction in femtoliter chamber array (invited), R. Iino: SANKEN WORKSHOP on Nano-Bioscience at Berkeley, Berkeley, USA, March 21-22, 2007.

Rapid detection of drug efflux from single bacterial cell enclosed in femtoliter chamber array (poster), R. Iino, K. Nishino, M. Nakata, E. Nikaïdo, Y. Matsumoto, S. Sakakihara, S. Takeuchi, A. Yamaguchi, and H. Noji: Micro Total Analysis Systems 2007, Paris, France, October 7-11, 2007.

ATP-driven Rotation of FoF1-ATP Synthase Reconstituted into Supported Membrane (poster), R. Iino, K. V. Tabata, H. Ueno, R. Hasegawa, and H. Noji: The Joint Biophysical Society 52nd Annual Meeting and 16th International Biophysics Congress, California, USA, 2-6 2008.

Versatile Acrylamide-based Microchambers for Single Molecular Biological Assays and Analysis (poster), L. Lam, S. Sakakihara, K. Ishizuka, S. Takeuchi, and H. Noji: Micro Total Analysis Systems 2007, Paris, France, October 7-11, 2007.

Fluorescence Imaging of Intracellular ATP Using A FRET-based Probe (poster), H. Imamura, K. Saito, K. P. H. Nhat, R. Iino, Y. Yamada, T. Nagai, and H. Noji: The Joint Biophysical Society 52nd Annual Meeting and 16th International Biophysics Congress, California, USA, 2-6 2008.

## **Contributions to International Conferences and Journals**

### **Publications in Domestic Meetings**

|                              |           |
|------------------------------|-----------|
| Biophysical Society of Japan | 11 papers |
| Japan Bioenergetics Group    | 4 papers  |
| Supported Membrane Workshop  | 2 papers  |

## **Academic Degrees**

### **Master Degree for Engineering**

R. Fujisawa      The role of substrate binding for the torque generation by

|           |                                                                                                                      |  |
|-----------|----------------------------------------------------------------------------------------------------------------------|--|
| M. Nakata | F <sub>1</sub> -ATPase<br>Measurement of activity of the drug efflux transporter by single cell fluorescence imaging |  |
|-----------|----------------------------------------------------------------------------------------------------------------------|--|

## Sponsorship

### Grant-in-Aid for Scientific Research on Priority Areas

|         |                                                                     |             |
|---------|---------------------------------------------------------------------|-------------|
| H. Noji | Rotational mechanism of F <sub>0</sub> F <sub>1</sub> -ATP synthase | ¥49,800,000 |
|---------|---------------------------------------------------------------------|-------------|

### Grant-in-Aid for Scientific Research (A)

|         |                                                                                                  |             |
|---------|--------------------------------------------------------------------------------------------------|-------------|
| H. Noji | Development of novel single molecule measurement method using ultra-small reaction chamber array | ¥15,600,000 |
|---------|--------------------------------------------------------------------------------------------------|-------------|

### Grant-in-Aid for Young Scientist (B)

|         |                                                                                       |          |
|---------|---------------------------------------------------------------------------------------|----------|
| R. Iino | Single molecule measurement of rotation of ATP synthase driven by proton motive force | ¥800,000 |
|---------|---------------------------------------------------------------------------------------|----------|

### Grant-in-Aid for JSPS Fellows

|            |                                                                                                               |            |
|------------|---------------------------------------------------------------------------------------------------------------|------------|
| H. Imamura | Rotational mechanism of V <sub>1</sub> -motor analyzed by single molecule technique and X-ray crystallography | ¥1,100,000 |
|------------|---------------------------------------------------------------------------------------------------------------|------------|

### Grant-in-Aid for JSPS Fellows

|         |                                                                                                    |            |
|---------|----------------------------------------------------------------------------------------------------|------------|
| H. Ueno | Single molecule rotational observation of F <sub>0</sub> -motor reconstituted into planar membrane | ¥1,100,000 |
|---------|----------------------------------------------------------------------------------------------------|------------|

### Grant-in-Aid for JSPS Fellows

|        |                                                           |          |
|--------|-----------------------------------------------------------|----------|
| L. Lam | Micro-device development for single molecule DNA analysis | ¥800,000 |
|--------|-----------------------------------------------------------|----------|

### Entrusted Research

|            |                                     |                                                  |            |
|------------|-------------------------------------|--------------------------------------------------|------------|
| H. Imamura | Japan Science and Technology Agency | Analysis of ATP metabolism by fluorescent probes | ¥3,695,000 |
|------------|-------------------------------------|--------------------------------------------------|------------|

### Other Research Fund

|         |       |                                                                                  |            |
|---------|-------|----------------------------------------------------------------------------------|------------|
| H. Noji | Atect | Development of device for rapid detection of bacteria that causes food-poisoning | ¥3,585,000 |
|---------|-------|----------------------------------------------------------------------------------|------------|

## Department of Cell Membrane Biology

|                                            |                                                                                                                                                                               |
|--------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Professor:                                 | Akihito YAMAGUCHI                                                                                                                                                             |
| Associate Professor:                       | Satoshi MURAKAMI                                                                                                                                                              |
| Research Associate:                        | Kunihiko NISHINO(2007.6.1-2007.3.31)                                                                                                                                          |
| Specially Appointed<br>Research Associate: | Syoko NISHI                                                                                                                                                                   |
| Post Doctoral Fellows:                     | Takashi MATSUMOTO, Yoshimi MATSUMOTO, Hidetada<br>HIRAKAWA(2007.4.1-2007.2.29)                                                                                                |
| Graduate Students:                         | Naoki KOBAYASHI, Satofumi HASHIMOTO, Ayumi<br>IWATA, Megumi OHIGASHI, Yu HISANO, Eiji NIKAIDO,<br>Li-Yuan WANG, Kosuke MIYATA, Mamiko ONOE, Hiroki<br>SAKATA, Tomoyuki NAKANO |
| Under Graduate Students:                   | Manami TANAKA                                                                                                                                                                 |
| Supporting Staff:                          | Kotoko ISE, Mari NISHIDA(2007.4.1-2007.12.31), Sumie<br>MATSUOKA(2007.7.6-2007.3.31)                                                                                          |

## Outlines

Xenobiotic extruding pumps have recently been known to be widely distributed in living organisms from mammalian to bacteria as a host-defense mechanism in cellular level. These pumps not only confer multidrug resistance of cancer cells and pathogenic bacteria but also cause hereditary diseases through the mutation. The purposes of our laboratory are to elucidate the molecular structures and the molecular mechanisms of these xenobiotic exporters and the roles of these exporters in cell functions. In addition, the exporters having xenobiotic exporter-like molecular structures are identified in brain and platelets in order to elucidate the possible roles of exporters in intercellular signal transduction.

We first determined the crystal structure of bacterial major xenobiotic exporter AcrB in 2002 and elucidated the molecular mechanism of xenobiotic export and the structural basis of multidrug recognition by determining the crystal structure of the drug-binding form of AcrB in 2006. In 2007, we continued to analyze crystal structures of the substrate-binding form of AcrB. In addition, we challenged to crystallize the other drug exporter TetA.

As for the regulation of xenobiotic exporter genes and the intrinsic physiological roles of bacterial xenobiotic exporters are also strictly studied as described below.

In addition, studies on the exporters for lipophilic signal transducers in mammalian cells have also been advanced as described below.

## Current Research Project

### **Crystallographic and protein engineering analysis of xenobiotic exporters.**

We have succeeded to determine the first crystal structure of bacterial multidrug efflux transporter AcrB in 2002. This is the first crystal structure for transporter proteins. Then we solved the structure of AcrB in complex with its substrates in 2006. The AcrB-substrate complex consists of three protomers, each of which represents one

functional state of transport cycle. Bound substrate was found in the periplasmic domain of one of the three protomers. The structure clearly revealed that drugs are exported by three-step functionally rotating ordered binding change mechanism. The multidrug recognition is revealed to be based on the multi-site binding of drugs. In 2007, we continued to solve the substrate-binding form of AcrB with different substrates. In addition, we tried to crystallize the other type of exporters such as TetA.

### **Studies on regulatory networks of xenobiotic exporters in *Salmonella enterica*.**

Xenobiotic exporters cause one major form of bacterial multidrug resistance and they also provide cells with a defense against toxic compounds in the environment. Previous studies have shown that *Salmonella enterica* serovar Typhimurium has at least nine xenobiotic exporters. This year, we report that bacterial metabolites induce the expression of these exporters. We found that indole, a major metabolite of *Escherichia coli*, induced expression of the xenobiotic exporters *acrAB*, *emrAB*, *acrD* and *mdtABC* in *Salmonella*. Among the products of these genes, AcrAB is especially effective in generating resistance and has wide substrate specificity. Genetic studies showed that a specific regulator in *Salmonella*, RamA, is required for indole to induce *acrAB*. In contrast, other known regulators of *acrAB* such as MarA, SoxS, Rob, SdiA and AcrR did not contribute to this induction. Furthermore, we found that RamA is responsible for the induction of *acrAB* and *tolC* by conditioned *E. coli* medium or by bile salts. RamA binds to upstream regions of *acrA* and *tolC*. These regions harbor binding sites for RamA to induce *acrAB* and *tolC* in response to indole, conditioned *E. coli* medium and bile salts. The evidence presented here suggests that the AcrAB-TolC xenobiotic exporter of *Salmonella* is induced in environments via the RamA regulator.

### **Characterization of the lipophilic signal transducing molecules export system in the mammalian cells.**

In addition to the stimuli-dependent sphingosine 1-phosphate (S1P) secretion from platelet, we found that the S1P was also secreted from the erythrocyte. However, secretion from erythrocyte did not require any stimulus. To determine the enzymatic properties of this S1P secretion system, we measured the S1P uptake activity into the rat erythrocyte inside-out vesicles. S1P was transported into the BSA preloaded vesicles by adding ATP. This uptake was inhibited with glyburide and vanadate but not with other inhibitors for transporters or ionophores. These results strongly suggested the presence of transporter mediated S1P export system in rat erythrocyte.

## **Publications**

### **Original Papers**

New Technique of Manipulating a Protein Crystal Using Adhesive Material, T. Kitatani, S. Sugiyama, H. Matsumura, H. Adachi, H. Y. Yoshikawa, S. Maki, S. Murakami, T. Inoue, Y. Mori and K. Takano: Applied Physics Express, 1 (3) (2008) 037002-1-3.

The AraC-family regulator GadX enhances multidrug resistance of *Escherichia coli* by activating expression of the *mdtEF* multidrug efflux genes, K. Nishino, Y. Senda and A. Yamaguchi: Journal of Infection and chemotherapy, 14 (1) (2008) 23-29.

Identification of a spermidine excretion protein complex (MdtJI) in *Escherichia coli*, K. Higashi, H. Ishigure, R. Demizu, T. Uemura, K. Nishino, A. Yamaguchi, K. Kashiwagi and K. Igarashi: *Journal of Bacteriology*, 190 (2) (2008) 872-878.

Tissue specific expression of the splice variants of the mouse vacuolar proton-translocating ATPase a4 subunit, S. Kawasaki-Nishi, A. Yamaguchi, M. Forgac and T. Nishi: *Biochemical and Biophysical Research Communications*, 364 (4) (2007) 1032-1036.

Regulation of multidrug efflux systems involved in multidrug and metal resistance of *Salmonella enterica* serovar Typhimurium, K. Nishino, E. Nikaido and A. Yamaguchi: *Journal of Bacteriology*, 189 (24) (2007) 9066-9075.

### **Review Papers**

Crystal Structure of a Multi-Drug Efflux Transporter Reveal a Functionally Rotating Mechanism, S. Murakami: *Seibutsu Butsuri*, 47 (2007) 309-316.

Structure and Function of Multi-Drug Transporters, S. Murakami: *Journal of The Surface Science Society of Japan*, 28 (2007) 184-191.

Molecular mechanism of multi-drug efflux protein, A. Yamaguchi: *Infection, Inflammation, Immunity*, 37 (2007) 106-115.

Structural basis of xenobiotic recognition by a bacterial xenobiotic exporter, S. Murakami and A. Yamaguchi: *The Journal of Biochemistry*, 79 (2007) 542-549.

Structure and Reaction Mechanism of Multi-Drug Efflux Transporter, S. Murakami: *PROTEIN, NUCLEIC ACID and ENZYME*, 52 (2007) 406-414.

Roles of Xenobiotic Transporters in Bacterial Drug Resistance and Virulence, K. Nishino: *Nippon Rinsho*, 65 (2007) 407-414.

Protein Crystallization Using Laser Irradiation, H. Adachi, Y. Mori, T. Sasaki, K. Takano, T. Inoue, H. Matsumura and S. Murakami: *JAPANESE JOURNAL of OPTICS*, 36 (2007) 10-14.

### **Patents**

Modulator for the receptor of autoinducer-2, N. Kato, M. Hiraoka, J. Ohkanda, T. Kawano, A. Yamaguchi, K. Nishino, S. Ebisu and Bonnie L. Bassler, tokugan 2007-056450

### **International Conferences**

Phenotypic analysis of multidrug efflux pumps - not just for multidrug resistance (invited), \*K. Nishino: *Florence Conference on Phenotype MicroArray Analysis of Microorganisms* (19-21 Mar. 2008, Florence, Italy).

Roles of multidrug efflux pumps in antimicrobial peptide resistance of *Salmonella*

enterica, \*T. Nakano, K. Nishino and A Yamaguchi: Florence Conference on Phenotype MicroArray Analysis of Microorganisms (19-21 Mar. 2008, Florence, Italy).

Regulatory network of AcrAB multidrug efflux pump in Salmonella and its role in response to metabolites, \*E. Nikaido, K. Nishino and A Yamaguchi: Florence Conference on Phenotype MicroArray Analysis of Microorganisms (19-21 Mar. 2008, Florence, Italy).

Structure and mechanism of bacterial multi-drug efflux systems, \*S Murakami: Gordon Research Conferences (NEW ANTIBACTERIAL DISCOVERY & DEVELOPMENT) (9-14 Mar. 2008, Il Ciocco Hotel and Resort Lucca (Barga), Italy).

Physiological functions of bacterial multidrug efflux pumps (invited), \*K. Nishino and A Yamaguchi: The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science (27-28 Feb. 2008, Chungnam National University, Korea).

Multidrug recognition and pumping by bacterial multidrug efflux transporter - A structural view (invited), \*S Murakami: Katzir Workshop on The Unbearable Complexity of Life(10-13 Feb. 2008, Tel Aviv University, Israel).

Structural Basis of Bacterial Multidrug Export, \*A Yamaguchi: 11<sup>th</sup> Sanken International Symposium/6th nanotechnology center international symposium/1st MSTEC international symposium(4-5 Feb. 2008, Hyogo).

Analysis of the S1P transporter in MEG-01 cell line (poster), \*Y. Hisano: 11<sup>th</sup> Sanken International Symposium/6th nanotechnology center international symposium/1st MSTEC international symposium(4-5 Feb. 2008, Hyogo).

Analysis of the expression site and the physiological role of mouse ABCA5 (poster), \*M. Ohigashi: 11<sup>th</sup> Sanken International Symposium/6th nanotechnology center international symposium/1st MSTEC international symposium(4-5 Feb. 2008, Hyogo).

Regulatory network of AcrAB multidrug efflux pump in Salmonella and its role in response to metabolites (poster), \*E. Nikaido: 11<sup>th</sup> Sanken International Symposium/6th nanotechnology center international symposium/1st MSTEC international symposium(4-5 Feb. 2008, Hyogo).

Structure and mechanism of bacterial multi-drug efflux systems (invited), \*S Murakami: International Symposium on Recent Trends in Macromolecular Structure and Function(7-11 Jan. 2008, Chennai, India).

Roles of indole signaling and intercellular signal transduction on type III secretion system-dependent pathogenicity in EHEC, \*H. Hirakawa, T. Kodama, T. Honda and A Yamaguchi: 3<sup>rd</sup> ASM Conference on Cell-Cell Communication in Bacteria (7-10 Oct. 2007, Texas, USA).

Visualization of Escherichia coli AcrAB-TolC efflux pump activity using ultra small

chambers (poster), \*Yoshimi Matsumoto, K. Nishino, R. Iino, S. Sakakihara, M. Nakata, H. Nojii and A Yamaguchi: 47<sup>th</sup> Interscience Conference on Antimicrobial Agents and Chemotherapy (Sep. 17-20, 2007, McCormick Place, Illinois USA).

Novel Aspects of Mechanisms of Antibacterial Resistance Revealed by Crystal Structure (invited), \*A Yamaguchi: 47<sup>th</sup> Interscience Conference on Antimicrobial Agents and Chemotherapy (Sep. 17-20, 2007, McCormick Place, Illinois USA).

Regulatory network of multidrug transporters reveals their physiological role in Salmonella virulence, \*K. Nishino, E. Nikaido, H. Sakata, T. Nakano, M. Tanaka and A Yamaguchi: 7<sup>th</sup> The Awaji International Forum on Infection and Immunity (Sep. 1-5, 2007, Awaji Yumebutai International Conference Center).

Regulatory network of multidrug transporters reveals their physiological role in Salmonella virulence (poster), \*K. Nishino, E. Nikaido, H. Sakata, T. Nakano, M. Tanaka and A Yamaguchi: 7<sup>th</sup> The Awaji International Forum on Infection and Immunity (Sep. 1-5, 2007, Awaji Yumebutai International Conference Center).

Regulation mechanisms of the acrAB multidrug efflux pump in Salmonella enterica in response to bacterial metabolites (poster), \*E. Nikaido, K. Nishino and A Yamaguchi: 7<sup>th</sup> The Awaji International Forum on Infection and Immunity (Sep. 1-5, 2007, Awaji Yumebutai International Conference Center).

Structure and mechanism of bacterial multi-drug efflux transporter, \*S Murakami: 24<sup>th</sup> European Crystallographic Meeting(22-27 Aug. 2007, Marrakech, Morocco).

Structure and mechanism of AcrAB bacterial multi-drug efflux pump, \*S Murakami: Seminar(21 Aug. 2007, Imperial College London, London, England).

Structure and mechanism of AcrAB bacterial multi-drug efflux pump (invited), \*S Murakami: AstraZeneca Membran Protein Day(Seminar) (20 Aug. 2007, Alderley Park, Macclesfield, UK).

Session1 Multi-Protein complex, Structural studies of multi-drug efflux transporter (invited), \*S Murakami: 9<sup>th</sup> International Conference on Biology and Synchrotron Radiation (13-17 Aug. 2007, Manchester, England).

Crystal structures of a bacterial multidrug transporter reveal a functionally rotating mechanism (invited), \*S Murakami: 32<sup>nd</sup> FEBS Congress, Molecular Machines (7-12 July 2007, Vienna, Austria).

Structure and mechanism of AcrAB bacterial multi-drug efflux pump, \*S Murakami: Seminar (25 May 2007, Scripps Inst., SanDiego).

Structure and mechanism of AcrAB bacterial multi-drug efflux pump, \*S Murakami: Seminar (24 May 2007, TakedaSD, SanDiego).



Structure and mechanism of AcrAB bacterial multi-drug efflux pump, \*S Murakami: Seminar (23 May 2007, Mpex Pharmaceuticals, Inc., SanDiego).

Structure and mechanism of AcrAB bacterial multi-drug efflux pump, \*S Murakami: Seminar (21-22 May 2007, UCSF, USA).

Single Cell Measurement of Bacterial Drug Efflux in Femtoliter Chamber Array (poster), \*K. Nishino, R. Iino, M. Nakata, Y. Matsumoto, E. Nikaido, S. Sakakihara, S. Takeuchi, A Yamaguchi and H. Noji: American Society of Microbiology, 107th General Meeting, (May 21-25, 2007, Metro Toronto Convention Center, Toronto, Canada).

Metabolites of Escherichia coli Induce the Expression of Multidrug Efflux Pumps in Salmonella enterica (poster), \*E. Nikaido, K. Nishino and A Yamaguchi: American Society of Microbiology, 107th General Meeting, (May 21-25, 2007, Metro Toronto Convention Center, Toronto, Canada).

### **Contributions to International Conferences and Journals**

A. Yamaguchi                      Journal of Bacteriology (Editorial Board Member)

#### **Publications in Domestic Meetings**

|                                                                                    |           |
|------------------------------------------------------------------------------------|-----------|
| 128 <sup>th</sup> The Pharmaceutical Society of Japan                              | 8 papers  |
| 81 <sup>th</sup> Japanese Society for Bacteriology                                 | 10 papers |
| Senri life science seminar                                                         | 1 paper   |
| SPRING-8 GPCR Symposium                                                            | 1 paper   |
| 45 <sup>th</sup> The Biophysical Society of Japan                                  | 1 paper   |
| The 30 <sup>th</sup> Annual Meeting of the Molecular Biology Society of Japan, The | 14 papers |
| 80 <sup>th</sup> Annual Meeting of the Japanese Biochemical Society                |           |
| 29 <sup>th</sup> Membrane-Drug Interaction Symposium                               | 4 papers  |
| 33 <sup>th</sup> Japanese Bioenergetics Group                                      | 2 papers  |
| 11 <sup>th</sup> Spring-8 Symposium                                                | 1 paper   |
| 12 <sup>th</sup> IMCB symposium, Structural biology of membrane transporters       | 1 paper   |
| 19 <sup>th</sup> Symposium on Microbial Sciences                                   | 4 papers  |
| 5th JHUPO Conference                                                               | 1 paper   |
| 4 <sup>th</sup> 21 <sup>st</sup> Century research conference on Escherichia coli   | 1 paper   |
| 6 <sup>th</sup> BIO FORUM JAPAN                                                    | 1 paper   |
| The 55 <sup>th</sup> Japanese Society of Chemotherapy                              | 2 papers  |

### **Academic Degrees**

#### **Doctor Degree for Pharmaceutical Sciences**

|              |                                                                                            |
|--------------|--------------------------------------------------------------------------------------------|
| N. Kobayashi | Identification of the membrane exporter that mediates secretion of sphingosine-1-phosphate |
| S. Hashimoto | Roles of novel RND-type membrane proteins on cholesterol homeostasis in mammalian cells    |

#### **Master Degree for Pharmaceutical Sciences**

|              |                                                                                                                                        |  |
|--------------|----------------------------------------------------------------------------------------------------------------------------------------|--|
| Li-Yuan Wang | Identification of novel gene products which play roles on biofilm formation in <i>Escherichia coli</i>                                 |  |
| E. Nikaido   | Investigation of the transcriptional regulation on xenobiotic exporter genes of <i>Salmonella</i> in response to environmental signals |  |
| K. Miyata    | Expression and cellular localization of ABCA6 in mouse liver                                                                           |  |
| M. Onoe      | Production and analysis of ABCA7 knockout mice                                                                                         |  |

## Sponsorship

### Grant-in-Aid for Scientific Research (S)

|              |                                                                                    |             |
|--------------|------------------------------------------------------------------------------------|-------------|
| A. Yamaguchi | Structures, functions, regulations and physiological roles of xenobiotic exporters | ¥18,000,000 |
|--------------|------------------------------------------------------------------------------------|-------------|

### Grant-in-Aid for Scientific Research (A)

|             |                                                                                 |            |
|-------------|---------------------------------------------------------------------------------|------------|
| S. Murakami | Analysis of efflux mechanism of RND-type transporter based on crystal structure | ¥7,200,000 |
|-------------|---------------------------------------------------------------------------------|------------|

### Grant-in-Aid for Young Scientists (S)

|            |                                                                                                                                       |             |
|------------|---------------------------------------------------------------------------------------------------------------------------------------|-------------|
| K. Nishino | Roles of orphan transporters in multidrug-resistant bacteria and development of therapeutic strategies to control infectious diseases | ¥12,700,000 |
|------------|---------------------------------------------------------------------------------------------------------------------------------------|-------------|

### Grant-in-Aid for Scientific Research on the Priority Area

|            |                                        |            |
|------------|----------------------------------------|------------|
| K. Nishino | Resistome analysis of bacterial genome | ¥4,700,000 |
|------------|----------------------------------------|------------|

### Grant-in-Aid for Young Scientists (B)

|          |                                                                                            |            |
|----------|--------------------------------------------------------------------------------------------|------------|
| S. Nishi | Investigation of novel role of V-ATPase isoforms on formation of intercellular environment | ¥1,800,000 |
|----------|--------------------------------------------------------------------------------------------|------------|

### Grant-in-Aid for JSPS Fellows

|             |                                                                                                                                                     |          |
|-------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| M. Ohigashi | Functional analysis of ABCA transporters for identification of the export system that mediates secretion of lipophilic signal transducing molecules | ¥900,000 |
|-------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|----------|

### Entrusted Research

|              |                                                                      |                                                                                                                              |             |
|--------------|----------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|-------------|
| A. Yamaguchi | Japan Science and Technology Agency (CREST)                          | Investigation of the Structure and Function for Xenobiotics Transporters and Clarification of Multidrug Resistance Mechanism | ¥3,023,000  |
| S. Murakami  | Ministry of Education, Culture, Sports, Science and Technology, MEXT | Structural biology on drug efflux transport machinery for overcoming multidrug resistance                                    | ¥23,307,000 |
| S. Murakami  | Japan Science and Technology Agency                                  | Creation of perfect protein crystals                                                                                         | ¥8,500,000  |

|              |                                                                                                                   |                                                                                                                                                                   |             |
|--------------|-------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| S. Murakami  | (CREST)<br>Japan Science and<br>Technology Agency<br>Strategic<br>international<br>cooperative<br>program/England | Clarification of multidrug<br>efflux mechanism based on<br>crystal structure of multidrug<br>transporter                                                          | ¥3,546,000  |
| A. Yamaguchi | The Program of<br>Founding Research<br>Centers for Emerging<br>and Reemerging<br>Infectious Diseases              | Exhaustive, systematic analysis<br>of bacterial pathogenicity and<br>transcriptional regulation of<br>multidrug transporters, and new<br>strategy for drug design | ¥300,000    |
| A. Yamaguchi | National Institute of<br>Biomedical<br>Innovation                                                                 | Development of novel<br>inhibitors that counteract<br>infectious diseases by drug<br>resistant bacteria                                                           | ¥75,385,000 |
| K. Nishino   | National Institute of<br>Animal Health                                                                            | Regulatory Networks of Drug<br>Resistance in <i>Escherichia coli</i>                                                                                              | ¥3,300,000  |
| K. Nishino   | Japan Science and<br>Technology<br>Agency • Sakigake                                                              | Roles of xenobiotic transporters<br>in cellular physiology                                                                                                        | ¥7,000,000  |

# Division of Quantum Beam Science & Technology

## Outline

The quantum beam is the general term for all kinds of radiation beams producing quantum mechanical effects on materials. It includes photon beams and charged particle beams such as lasers, X-rays, synchrotron radiation,  $\gamma$ -rays and free electron lasers, electrons, positrons, muons and ions, as well as neutron beams. Quantum beam science has developed from radiation science and its research fields are classified into two groups. One of them is study on production, control and measurement of new high-brightness and high quality quantum beams, which are remarkably developing recently. The other is study on processes induced by quantum beams in materials, as well as on applications to materials science based on accurate understanding of these phenomena induced by a quantum beam.

The division of Quantum Beam Science and Technology is composed of the department of Accelerator Science and the department of Beam Materials Science. In the department of Accelerator Science, studies are conducted on accelerators, which are main apparatuses for producing quantum beams, and on production, control and measurement of quantum beams using accelerators. In the department of Beam Materials Science, basic studies are conducted to investigate phenomena induced by quantum beams and to apply them to materials science; that is, production and application of new materials such as functional materials and materials working under extreme conditions. Both departments closely work together with different points of view; generation of new quantum beams and applications of them to materials science. This division also cooperates with the Radiation Laboratory, attached to the Nanotechnology center, in order to promote advanced studies with a different point of view from that of national laboratories. Furthermore we plan to actively promote researches to develop and use high-performance accelerators suitable for producing new kinds of high-brilliant and high-quality beams and for applying to materials science, which are being developed or under construction in this country as well as abroad.

## Achievements

- Two 108 MHz RF cavities are fabricated for the SHB system of the L-band electron linac. As a result of replacement of the SHB system with the three new RF cavities of high performance, including a 216 MHz SHB cavity made last year, stability of the single bunch and the multi-bunch operation modes is significantly improved.
- Amplitude and phase variations of the output RF power from the klystron over the RF pulse are reduced to 0.89 % and 0.3 degrees, respectively, with the feed forward control and we succeed in accelerating a multi-bunch electron beam with a small energy spread.
- The far-infrared FEL is re-commissioned after long suspension and we succeeded

in high power operation of FEL at 70  $\mu\text{m}$  wavelength reaching power saturation for the first time.

- A new instrument is developed to directly measure the electron distribution of the electron beam in the phase space consisting of energy and time.
- As a part of development of high performance wiggler for SASE, directional errors of magnetization are systematically measured for 80 magnet blocks.
- Analysis of primary process in interactions between beams and molecular/polymer materials.
- Development of ultrafast measurement system using electron and photon pulse.
- Electronic structure and physical properties of  $\sigma$ - and  $\pi$ -conjugated polymer materials.
- Reaction mechanisms in polymeric materials for microelectronics.
- Formation of size-controlled nano-wires along particle trajectories in polymeric materials.
- Electrodeless measurement of conductivity in organic semiconductors by microwave technique.
- Ionizing radiation induced damages in DNA.

## Department of Accelerator Science

|                      |                                  |
|----------------------|----------------------------------|
| Professor:           | Goro ISOYAMA                     |
| Associate Professor: | Ryukou KATO                      |
| Assistant Professor: | Toshiji IKEDA, Shigeru KASHIWAGI |
| Graduate Student:    | Yutaka MORIO                     |

### Outline

Particle accelerators are widely used from basic science to industrial applications. In this department, we conduct research on accelerators and quantum beams such as a free electron laser (FEL). Although accelerators are artificial things, fundamental aspects of physics such as non-linearity and the collective effect become apparent when extreme performance is pursued. Because new kinds of quantum beams extend the world we can see with, they are expected to be used in a large variety of fields extending from basic research to applications. To put it concretely, we conduct researches on production of a highly brilliant electron beam with a linear accelerator and related beam dynamics, development of an infrared FEL for user experiments and SASE (Self-Amplified Spontaneous Emission) in the infrared region.

### Current Research Projects

#### Upgrade of the L-band Linac

In the single-bunch and the multi-bunch modes, for which the sub-harmonic buncher (SHB) system consisting of three RF cavities is used, warm-up operation for longer than 4 hours is necessary to begin experiment in the morning. A state of the electron beam sometime and suddenly changes besides. These problems are due to the facts that the SHB cavities are made of a cladding plate of stainless steel on copper and that a heating place by dissipation of the RF power in a cavity is apart from a water-cooling place. For highly stable operation of the linac in the single-bunch and multi-bunch modes, we began a project to renew the sub-harmonic buncher (SHB) system consisting of three RF cavities last year. Since temperature stability of the RF cavities is essential to stabilization of the electron beam, the RF cavities are made only of oxygen-free copper, which has higher thermal conductivity than the clad plate of stainless steel on copper previously used, and the special design is adopted to cool main parts effectively with water. The effective and highly stable cooling system is realized so that several long holes of 5 mm in diameter are drilled along the beam axis in the outer and the inner conductors made of oxygen-free copper and that cooling water with temperature stability of 0.01 °C is run through the holes. As the first step, a 216 MHz quarter wavelength cavity was designed and fabricated. In succession, we made two 108 MHz cavities this year. We have replaced the old SHB cavities with the new ones, including the 218 MHz cavity made last year. After commissioning of the new SHB system, it is used for joint-use experiments of the L-band linac without any problems. It is possible to begin experiments in much shorter time than before after start-up in the morning.

In then multi-bunch mode operation used for FEL, it is necessary to accelerate a long pulse electron beam with a small energy spread. The amplitude and the phase of the

pulsed RF power provided to the linac have to be constant over the pulse duration of 8  $\mu\text{s}$ . For the purpose, ripples of the flat-top in the high voltage square pulse applied to the klystron, which generates the RF power for the linac, are reduced to 0.1 %, but the amplitude varies by 10.5 % and the phase by larger than 5 degrees on the flat-top of the RF pulse. These variations of the amplitude and the phase affect the energy spectrum of the accelerated electron beam and hence it is not possible to accelerate electron beams with the small energy spread in the multi-bunch mode. In order to solve this problem, we are conducting research on stabilization of the amplitude and the phase in the RF pulse by the feed-forward method. The method is applied to the output RF pulse from a klystron with phase variations of 13 degrees and amplitude variations of 18 % in the duration of 7.6  $\mu\text{s}$ , so that the variations are reduced to 0.3 degrees in phase and 0.89 % in amplitude. In order to study effects of the phase and the amplitude variations on electron beam acceleration, energy spectra of electron beams are measured with and without the feed forward compensation. Energy variations over 5 $\mu\text{s}$  are reduced from 6.9 % without the phase and amplitude compensation to 0.45 % with the compensation.

When the operation mode of the klystron modulator is changed and a beam profile monitor is used, a linac operator manually operates a preset scaler module made by Kaizu Works (KN-140) that determines the operation cycle of the linac to change the repetition rate of the RF pulse or the beam. In order to prevent accidents by mistake, we have developed a new preset scaler that can be connected to a personal computer for control with USB interface. We have also modified the control software to incorporate the new device in the computer control system. An operation test of the device and a control test from the personal computer have been completed, and it is waiting for a synthetic test of the control system for daily use.

### **Production and Measurement of Highly Brilliant Electron Beams**

We are conducting research and development of a phase space monitor, with which the electron distribution can be directly measured on the phase space defined by the accelerating energy and the time of the L-band linac. The energy of the electron beam is dispersed after passing through a bending magnet. Cherenkov light is emitted when the electron beam goes through the material called aerogel, which has the refractive index slightly higher than that of the air, and the emitted light is measured with a streak camera. If the streak axis is taken perpendicular to the energy axis, the phase space distribution of the electron beam is reconstructed on the display screen of the streak camera. When hydrophobic silica-aerogel with the refractive index  $n = 1.050$  is used, Cherenkov light is emitted on a cone with an almost constant opening angle with respect to the electron beam axis for electron energy above 10 MeV, 17.75 degrees. Because it is difficult to concentrate all the Cherenkov light with such a large divergence angle, portion of it is sliced out with a focusing mirror. A 1.5 mm thick aerogel is stuck on a metal mirror, which also works as a mechanical support for the aerogel, and the mirror with aerogel is inclined to the beam axis by 55.8 degrees so that the upper-most part of Cherenkov light is taken out to the upward direction. Cherenkov light emitted in the aerogel and then reflected by the mirror passes through the aerogel again and it is taken out in the vacuum. We have made such an apparatus and have installed on the FEL beam line. We are ready to measure the phase space distribution of the electron beam.

### **Development of the Far-Infrared Free Electron Laser**

We have been developing a far-infrared free electron laser (FEL) using the L-band electron linac at ISIR, Osaka University. Since the success in the first FEL lasing at wavelengths 32~40  $\mu\text{m}$  in 1994, we conducted research to expand the wavelength region towards the longer wavelength side, and succeeded in lasing at 150  $\mu\text{m}$  in 1998, which was the longest wavelength ever obtained with an FEL based on an RF linac. The L-band electron linac was not designed for FEL and hence it was not possible to accelerate an electron beam with a long pulse duration necessary for high power operation of FEL. The linac was, furthermore, constructed approximately 30 years ago and stability and reproducibility of the linac operation were not sufficient enough. The FEL could not be used for users experiments and we suspended FEL experiments for a while. The budget was approved in 2002 for large-scale remodeling of the L-band electron linac and we renewed the linac to improve stability and reproducibility of the linac. We, on that occasion, added a function to a klystron modulator to produce a long pulse electron beam for high power operation of FEL. We succeeded in accelerating a multi-bunch electron beam with a small energy spread by correcting the phase and the amplitude of the RF power by the feed forward method so that they are constant over the long pulse duration. We re-commissioned the FEL system in August 2007 and obtained saturation of the FEL power at a wavelength 70  $\mu\text{m}$ . We are currently conducting FEL experiments in the wavelength region 70~110  $\mu\text{m}$  by changing the electron beam energy and the magnetic field of the wiggler.

#### **Development of a High Performance Wiggler for SASE**

We are conducting research on measurement and evaluation of characteristics of permanent magnet materials, which are one of the bases for realizing high performance wigglers for SASE and FEL. The permanent magnet material we use is the compound of neodymium, iron, and boron. Powdery raw materials are compressed and shaped under the strong magnetic field to be raw blocks. They are sintered and then machined down to specified dimensions. The finished blocks are magnetized again in the magnetic field and permanent magnet blocks are completed. The main characteristics of permanent magnet such as the magnetic field strength, the direction of the magnetization axis, and the uniformity of magnetization depend not on the final magnetization but on the first process for compression and shaping under the magnetic field. We are conducting basic study to produce ideal magnet blocks without magnetization errors in direction and in strength by devising how to cut magnet blocks out of raw material. In order to investigate the method, it is necessary to measure the magnetic field distribution on the surface of magnetized raw blocks. We measured magnetization directions and surface magnetic field distributions of 80 magnet blocks made for test. It is found that directions of the magnetization axis are inclined to the zero degree direction of the compass and distributed around the central angular error of 0.2 degrees. We will continue research on fabrication of high quality permanent magnet blocks.

#### **Publications**

##### **Original Papers**

Study of Compton Backscattering Between Relativistic Electron Beam and SASE Light, S. Kashiwagi, R. Kuroda: Int. J. Mod. Phys. B, 21 (2007) 481-487.



Improvements in time resolution and signal-to-noise ratio in a compact pico-second pulse radiolysis system, Hiroyuki Nagai, Masaaki Kawaguchi, Kazuyuki Sakaue, Keita Komiya, Tomoaki Nomoto, Yoshio Kamiya, Yoshimasa Hama, Masakazu Washio, Kiminori Ushida, Shigeru Kashiwagi and Ryunosuke Kuroda: Nucl. Instrum and Methods B, 265 (2007) 82-86.

Involvement of Histamine Released From Mast Cells in Acute Radiation Dermatitis in Mice, Saiko Moriyasu, Kouichi Yamamoto, Naoko Kureyama, Keita Okamura, Toshiji Ikeda, Atsushi Yamatodani: Journal of Pharmacological Sciences, 104 (2007) 187-190.

Electrical insulating property of ceramic coating materials in radiation and high-temperature environment, Teruya Tanaka, Rei Nagayasu, Akihiko Sawada, Toshiji Ikeda, Fuminobu Sato, Akihiro Suzuki, Takeo Muroga, Toshiyuki Iida: Journal of Nuclear Materials, 367-370 (2007) 1155–1159.

### **Review Papers**

Electrical insulating properties of ceramic coating materials for liquid Li blanket system under irradiation (in Japanese), T. Tanaka, T. Muroga, T. Shikata, B. Tsuchiya, M. Narui, T. Nishitani, T. Iida, F. Sato, T. Ikeda, A. Suzuki, J. Japan Soc. Plasma Sci. Nucl. Fusion Res. Vol. 83, No. 4 (2007) 391-396.

### **International Conferences**

Control system based on PCs and PLCs for the L-band linac at Osaka University (poster), Ryukou Kato, Shigeru Kashiwagi, Tamotsu Yamamoto, Shoji Suemine, \*Goro Isoyama: Asian Particle Accelerator Conference 2007, Indore, INDIA, January 29 - February 2, 2007.

New Timing System for the L-band Linear Accelerator at Osaka University (poster), S. Kashiwagi, \*G. Isoyama, R. Kato, S. Suemine, T. Asaka, Y. Kawashima: Asian Particle Accelerator Conference 2007, Indore, INDIA, January 29 - February 2, 2007.

Development of compact EUV source based on laser Compton scattering (poster), \*S. Kashiwagi, R. Kato, J. Yang, A. Masuda, T. Nomoto, T. Gowa, K. Sakaue, M. Washio, R. Kuroda, J. Urakawa: 2007 Particle Accelerator Conference, New Mexico, USA, June 25-29, 2007.

Development of Photocathode RF Gun and Laser System for Multi-collision Laser Compton Scattering (poster), \*R. Kuroda, H. Toyokawa, M. Yasumoto, N. Sei, H. Ogawa, M. Koike, K. Yamada, T. Nakajyo, F. Sakai, T. Yanagida, T. Gowa, A. Masuda, R. Moriyama, Y. Kamiya, K. Sakaue, M. Washio, S. Kashiwagi: 2007 Particle Accelerator Conference, New Mexico, USA, June 25-29, 2007.

Improvement of Soft X-ray Generation System Based on Laser Compton Scattering (poster), \*T. Gowa, A. Masuda, R. Moriyama, K. Sakaue, Y. Kamiya, M. Washio, S. Kashiwagi, Ushida, H. Hayano, J. Urakawa: 2007 Particle Accelerator Conference, New Mexico, USA, June 25-29, 2007.

RE-COMMISSIONING OF THE FAR-INFRARED FREE ELECTRON LASER FOR STABLE AND HIGH POWER OPERATION AFTER THE RENEWAL OF THE L-BAND LINAC AT ISIR, OSAKA UNIVERSITY, \*R. Kato, S. Kashiwagi, T. Igo, Y. Morio, G. Isoyama: 29th International Free Electron Laser Conference, Novosibirsk, Russia, August 26 - 31, 2007.

DEVELOPMENT OF THE LONGITUDINAL PHASE-SPACE MONITOR FOR THE L-BAND ELECTRON LINAC AT ISIR, OSAKA UNIVERSITY (poster), \*R. Kato, S. Kashiwagi, T. Igo, Y. Morio, G. Isoyama: 29th International Free Electron Laser Conference, Novosibirsk, Russia, August 26 - 31, 2007.

DEVELOPMENT OF A PRECISE TIMING SYSTEM FOR THE ISIR L-BAND LINAC AT OSAKA UNIVERSITY (poster), Shigeru Kashiwagi, Goro Isoyama, \*Ryukou Kato, Shoji Suemine: 29th International Free Electron Laser Conference, Novosibirsk, Russia, August 26 - 31, 2007.

Re-Commissioning and High Power Operation of the Free Electron Laser in the Far-Infrared Region at ISIR, Osaka University (poster), \*Goro Isoyama, Ryukou Kato, Shigeru Kashiwagi, Tetsuya Igo, Yutaka Morio: 11th SANKEN International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Longitudinal Phase-Space Measurements of the High-Brightness Electron Beam at ISIR, Osaka University (poster), Ryukou Kato, Shigeru Kashiwagi, Tetsuya Igo, Yutaka Morio, \*Goro Isoyama: 11th SANKEN International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

X-Ray Microbeam Measurement with Radiophotoluminescent Glass for Singlecell Irradiation (poster), \*Sato, F., Kuchimaru, T., Ikeda, T., Shimizu, K., Kato, Y., Yamamoto, T. & Iida, T.: 15th International Conference on Solid State Dosimetry July 8-13, 2007 Delft, The Netherlands.

#### **Publications in Domestic Meetings**

|                                                                                            |           |
|--------------------------------------------------------------------------------------------|-----------|
| Annual Meeting of Particle Accelerator Society of Japan and the Linear Accelerator Meeting | 10 papers |
| Annual Meeting of the Japanese Society for Synchrotron Radiation Research                  | 3 papers  |
| Annual Meeting of the Physical Society of Japan                                            | 3 papers  |
| Scientific Meeting of the Japanese Society of Radiation Safety Management                  | 4 papers  |
| Annual Meeting of the Japanese Society of Snow and Ice                                     | 2 papers  |

#### **Academic Degrees**

## **Sponsorships**

### **Grant-in-Aid for Scientific Research (C)**

|         |                                                                                        |          |
|---------|----------------------------------------------------------------------------------------|----------|
| R. Kato | Development of the longitudinal phase-space monitor for high-brightness electron beams | ¥800,000 |
|---------|----------------------------------------------------------------------------------------|----------|

## Department of Beam Materials Science

Professor: Seiichi TAGAWA  
Associate Professor: Shu SEKI (until September)  
Assistant Professor: Kazuo KOBAYASHI, Akinori SAEKI  
Appointed Assistant Professor: Hiroki YAMAMOTO (from 16<sup>th</sup> January)  
Appointed Professor: Kazuyuki HORIE  
Research Students: Kikuo FURUKAWA  
Graduate Students: Hiroki YAMAMOTO, Yoshiko KOIZUMI,  
Ryuhei YAMAGAMI,  
Ryo HIROSE, Takehiro FUKUYAMA, Masafumi TANAKA  
Under Graduate Students: Shin-ichi OHSAKI  
Supporting Staff: Kaoru KOJIMA

### Outline

Main subjects of the present department are utilization of quantum beams for molecular science, research on mechanisms of phenomena induced by quantum beams, and analysis of microscopic structure of materials. Quantum beams mean both beams such as photons and beams inducing interactions with materials in the microscopic level of quantum mechanics. The beams cause completely different physico-chemical reactions in condensed matters from conventional chemical reactions. Features of beams are highly developed for electrons, ions, positrons, as well as photons (synchrotron radiation, gamma-rays, and lasers).

### Current Research Projects

#### 1. Analysis of Primary Process in Interactions between Beams and Molecular Materials

Physico-chemical reactions, which occur within nano- and pico- second region, are considered to dominate followed reactions and products in molecular materials. In the previous year, high-accuracy spectrum acquisition system was developed using CCD camera, highly-stable femtosecond white light continuum, and double pulse detection technique, resulting in approximately two orders of magnitude higher performance than conventional system. Using this system, the direct observation of reactive intermediates is carried out to elucidate the mechanisms and to control the reaction. For example, the reactivity of presolvated and solvated electrons in tetrahydrofuran were investigated, demonstrating the former has high reactivity and forms radical anions of solute which were quantitatively assessed by detecting the transient photoabsorption spectrum. Aromatics have high radiation resistance. The characteristic has been used in electron beam lithography. Especially, the radiation-induced reaction of aromatics is important to improve and understand the resist materials. Primary process of irradiated aromatics from nano- to picosecond time scale is investigated by electron beam pulse radiolysis.

#### 2. Development of Ultrafast Measurement System Using Electron and Photon

## **Pulses**

The measurement system was developed to trace ultrafast phenomena by ultra short pulses of electrons and photons in the current program. Transient spectroscopy is done within 0.8 psec approaching to shorter time region. Dynamics of short-lived intermediates have been observed for several molecular materials.

### **3. Electronic Structure and Physical Properties of $\sigma$ -and $\pi$ -Conjugated Polymers**

Polysilanes and polygermanes containing only silicon and germanium in the backbone are attached considerable attention because of their interesting electro-optical properties which are due to conjugated bondings in the main chain. The electronic structure of conjugated skeleton is investigated in the present program, which leads to improve the physical properties of the conjugated polymers. The optical properties of one-electron oxidized or reduced states of oligofluorenes, which are one of the most famous p-conjugated molecules, were investigated by nanosecond pulse radiolysis. It was found that the anion radical shows a planar structure by delocalizing the excess electron, which was also supported by density functional theory.

### **4. Reaction Mechanisms in Polymeric Materials for Microelectronics**

Chemically amplified resist system is one of the most practical candidates in the future technology in semiconductor fabrication. Reaction mechanisms in the system are analyzed upon exposure to electron beams, EUV, and laser beams to design newly developed lithography technique in the present program. We focused on the time evolutions of spatial distribution of chemical intermediates such as proton, radical cation, electrons, and counter anion, which were measured by picosecond pulse radiolysis technique.

### **5. Electrodeless measurement of conductivity in organic semiconductors by microwave technique**

Using time-resolved microwave conductivity (TRMC) which enables us to measure nano-scale electric conductivity in organic semiconductors, we investigated electric and optical properties of super-molecular nanotubes, and sigma or pi-conjugated polymer: polysilane. Regarding the super-molecular nanotube, anisotropic charge carrier mobility along the long axis of the nanotube was successfully measured. Moreover, the nanotube laminated by electron acceptor layers was found to show extraordinary conductivity, due to its programmed structure on nano-scale. The co-assembly of acceptor-bound molecules and normal molecules demonstrated higher optoelectronic properties than the nanotubes that consist from one type of molecule. A porphyrin-C60 crystal was proved to show a high capability of electron transport, demonstrates the plausibility of organic crystals as the use of high efficiency electronic devices.

### **6. Ionizing Radiation Induced Damage in DNA**

The dynamics of guanine cation radical ( $G^{+\frac{3}{4}}$ ) in oligonucleotides (ODNs) was measured spectroscopically by nanosecond pulse radiolysis. The one-electron oxidation of ODN produced  $G^{+\frac{3}{4}}$ , followed by deprotonation to yield the neutral G radical

( $\text{G}(-\text{H})^{\frac{3}{4}}$ ). The characteristic absorption maxima of  $\text{G}^{+\frac{3}{4}}$  around 400 nm were shifted to a longer wavelength in the order of  $\text{G} < \text{GG} < \text{GGG}$ -containing ODNs. In contrast, the spectra of  $\text{G}(-\text{H})^{\frac{3}{4}}$  were not affected by the sequence and were essentially similar to that of free dG. These results suggest that the positive charge in  $\text{G}^{+\frac{3}{4}}$  in ODN is delocalized over the extended  $\pi$  orbitals of DNA base. The rate constant of the deprotonation was altered by the sequence of ODNs, where bases adjacent to guanine are important factors for deprotonation.

## Publications

### Original Papers

Formation of isolated ultrafine optical nanofibers by single particle nanofabrication technique, K. Maehashi, H. Ozaki, Y. Ohno, K. Inoue, K. Matsumoto, S. Seki, and S. Tagawa: Appl. Phys. Lett., 90 (2) (2007) 23103-23106.

Effects of Porphyrin Substituents on Film Structure and Photoelectrochemical Properties of Porphyrin/Fullerene Composite Clusters Electrophoretically Deposited on Nanostructured SnO<sub>2</sub> Electrodes, H. Imahori, M. Ueda, S. Kang, H. Hayashi, S. Hayashi, H. Kaji, S. Seki, A. Saeki, S. Tagawa, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, M. Shiro, N. V. Tkachenko, H. Lemmetyinen: Chem. Eur. J., 13 (36) (2007) 10182-10193.

Electric Field Enhancement of Nano Gap of Silver Prisms, K. Yamaguchi, T. Inoue, M. Fujii, M. Haraguchi, T. Okamoto, M. Fukui, S. Seki, \*S. Tagawa: Chin. Phys. Lett., 24 (10) (2007) 2934-2937.

Molecular Engineering of Coaxial Donor-Acceptor Heterojunction by Coassembly of Two Different Hexabenzocoronenes: Graphitic Nanotubes with Enhanced Photoconductive Properties, Y. Yamamoto, T. Fukushima, A. Saeki, S. Seki, S. Tagawa, N. Ishii, T. Aida: J. Am. Chem. Soc., 129 (30) (2007) 9276-9277.

Exposure dose dependence on line edge roughness of a latent image in electron/extreme ultraviolet lithographies studied by Monte Carlo technique, A. Saeki, T. Kozawa, S. Tagawa, H. B. Cao, H. Deng, M. J. Leeson: J. Micro/Nanolith. MEMS MOEMS, 6 (2007).

Dynamics of photogenerated charge carrier and morphology dependence in polythiophene films studied by in situ time-resolved microwave conductivity and transient absorption spectroscopy, A. Saeki, S. Seki, Y. Koizumi, S. Tagawa: J. Photochem. Photobiol. A, 186 (2) (2007) 158-165.

Formation of isolated ultrafine optical nanofibers by single particle nanofabrication technique, S. Seki, S. Tsukuda, S. Tagawa, M. Sugimoto, A. Watanabe, T. Miyashita: J. Photopolym. Sci. Technol., 20 (1) (2007) 125-128.

Resist removal by using wet ozone, H. Horibe, M. Yamamoto, T. Ichikawa, T. Kamimura, S. Tagawa: J. Photopolym. Sci. Technol., 20 (2) (2007) 315-318.

Sensitization Distance and Acid Generation Efficiency in a Model System of Chemically Amplified Electron Beam Resist with Methacrylate Backbone Polymer, T. Kozawa, S. Tagawa, T. Kai, T. Shimokawa: J. Photopolym. Sci. Technol., 20 (4) (2007) 577-583.

Reactivity between Biphenyl and Precursor of Solvated Electrons in Tetrahydrofuran Measured by Picosecond Pulse Radiolysis in Near-Ultraviolet, Visible, and Infrared, A. Saeki, T. Kozawa, Y. Ohnishi, S. Tagawa: J. Phys. Chem. A, 111 (7) (2007) 1229-1235.

Possibility of reverse Monte Carlo modelling for hydrogenated amorphous Si deposited on reactive ion etched Si substrate, T. Kawahara, Y. Matsui, S. Tagawa, T. Kawai, H. Matsumura: J. Phys. Condens. Matter, 19 (33) (2007) 335211-335200.

Analysis of swelling process of protein by positron annihilation lifetime spectroscopy and differential scanning calorimetry, Y. Akiyama, Y. Shibahara, S. Takeda, Y. Izumi, Y. Honda, S. Tagawa, S. Nishijima: J. Polym. Sci. B, 45 (15) (2007) 2031-2037.

Dissolution characteristics and reaction kinetics of molecular resists for extreme-ultraviolet lithography, M. Toriumi, J. J. Santillan, T. Itani, T. Kozawa, S. Tagawa: J. Vac. Sci. Technol. B, 25 (6) (2007) 2486-2489.

Image contrast slope and line edge roughness of chemically amplified resists for postoptical lithography, T. Kozawa, S. Tagawa, J. J. Santillan, M. Toriumi, T. Itani: J. Vac. Sci. Technol. B, 25 (6) (2007) 2295-2300.

Stroboscopic Picosecond Pulse Radiolysis Using Near-Ultraviolet-Enhanced Femtosecond Continuum Generated by CaF<sub>2</sub>, A. Saeki, T. Kozawa, K. Okamoto, S. Tagawa: Jpn. J. Appl. Phys., 46 (1) (2007) 407-411.

Dependence of Absorption Coefficient and Acid Generation Efficiency on Acid Generator Concentration in Chemically Amplified Resist for Extreme Ultraviolet Resists, R. Hirose, T. Kozawa, S. Tagawa, T. Kai, T. Shimokawa: Jpn. J. Appl. Phys., 46 (40) (2007) L979-L981.

Theoretical Study on Relationship between Acid Generation Efficiency and Acid Generator Concentration in Chemically Amplified Extreme Ultraviolet Resists, T. Kozawa, S. Tagawa, M. Shell: Jpn. J. Appl. Phys., 46 (47) (2007) L1143-L1145.

Point Spread Function for the Calculation of Acid Distribution in Chemically Amplified Resists Used for Electron-Beam Lithography, T. Kozawa, S. Tagawa: Jpn. J. Appl. Phys., 46 (48) (2007) L1200-L1202.

Scanning Tunneling Microscopy Profiling of Steep Ridges Using Metal-Coated Carbon Nanotube Tip, Y. Murata, M. Kishida, K. Motoyoshi, T. Kimura, S. Honda, K. Okamoto,

Y. Matsui, S. Tagawa, M. Katayama: Jpn. J. Appl. Phys., 46 (12) (2007) 8005-8007.

Polymer-Structure Dependence of Acid Generation in Chemically Amplified Extreme Ultraviolet Resists, H. Yamamoto, T. Kozawa, S. Tagawa, H. B. Cao, H. Deng, M. J. Leeson: Jpn. J. Appl. Phys., 46 (7) (2007) L142-L144.

Single-Component Chemically Amplified Resist Based on Dehalogenation of Polymer, H. Yamamoto, T. Kozawa, S. Tagawa, K. Ohmori, M. Sato, H. Komano: Jpn. J. Appl. Phys., 46 (26) (2007) L648-L650.

Study of Acid-Base Equilibrium in Chemically Amplified Resist, K. Natsuda, T. Kozawa, A. Saeki, K. Okamoto, S. Tagawa, K. Ohmori, M. Sato, H. Komano: Jpn. J. Appl. Phys., 46 (11) (2007) 7285-7289.

Effect of Acid Diffusion and Polymer Structure on Line Edge Roughness, H. Yamamoto, T. Kozawa, A. Saeki, K. Okamoto, S. Tagawa, K. Ohmori, M. Sato, H. Komano: Jpn. J. Appl. Phys., 46 (10) (2007) 6187-6190.

Optoelectronic properties and nanostructure formation of sigma-conjugated polymers, S. Seki, S. Tagawa: Polym. J., 39 (4) (2007) 277-293.

Study of annihilation processes of positrons in polystyrene-related polymers, Y. Honda, T. Shimada, M. Tashiro, N. Kimura, Y. Yoshida, G. Isoyama, S. Tagawa: Radiat. Phys. Chem., 76 (2) (2007) 169-171.

Subpicosecond pulse radiolysis in liquid methyl-substituted benzene derivatives, K. Okamoto, T. Kozawa, A. Saeki, Y. Yoshida, S. Tagawa: Radiat. Phys. Chem., 76 (5) (2007) 818-826.

Ion beam induced nano-space reactions and nano-wire formation in polymers by high energy sub  $\mu$  m heavy ion beams, S. Tagawa, S. Tsukuda, S. Seki, M. Sugimoto, T. Sato, M. Oikawa, T. Sakai: Surf. Coat Tech, 201 (19) (2007) 8495-8498.

Nanowires with controlled sizes formed by single ion track reactions in polymers, S. Tsukuda, S. Seki, M. Sugimoto, S. Tagawa: Surf. Coat Tech, 201 (19) (2007) 8526-8530.

Cross-linked silicon based polymer nano-wire formation by high energy charged particles, S. Seki, S. Tsukuda, S. Tagawa, M. Sugimoto: Surf. Coat Tech, 201 (19) (2007) 8486-8489.

In vitro preparation of iron-substituted human manganese superoxide dismutase: Possible toxic properties for mitochondria, F. Yamakura, K. Kobayashi, S. Furukawa, Y. Suzuki: Free Radical Biology and Medicine, 43 (3) (2007) 423-430.

## Review Papers



## Books

### International Conferences

Electric Field Enhancement of Nano Gap of Silver Prisms (poster), K. Yamaguchi, T. Inoue, M. Fujii, M. Haraguchi, T. Okamoto, S. Seki, \*S. Tagawa: Asian and Pacific Symposium on Radiation Chemistry.

High Precision Measurement of Higher Diffraction-order Contamination in Monochromatized Soft X-ray by using a Compact Transmission-Grafting Spectrometer (poster), K. Fukui, T. Sakai, T. Hatsui, N. Kosugi, Y. Hamamura, K. Okamoto, Y. Matsui, T. Kozawa, S. Seki, \*S. Tagawa: International Conference on Vacuum Ultraviolet Radiation Physics.

Effect of Fluorine Atom on Acid Generation in Chemically Amplified EUV Resists (poster), \*H. Yamamoto, T. Kozawa, S. Tagawa, H. Yukawa, M. Sato, H. Komano: EUVL Symposium.

Single-Component Chemically Amplified Resist Based on Dehalogenation of Polymer (poster), \*H. Yamamoto, T. Kozawa, S. Tagawa, K. Ohmori, M. Sato, H. Komano: SPIE.

Development and Performance of Quasi-Free Standing Transmission-Grating for Soft X-ray Emission Spectrometer (poster), H. Takai, \*K. Okamoto, M. Matsui, T. Kozawa, S. Seki, S. Tagawa, Y. Hamamura, N. Kosugi: International Conference on Vacuum Ultraviolet Radiation Physics.

Pulse Radiolysis of Polystyrene and Derivatives (poster), \*K. Okamoto, M. Tanaka, S. Seki, T. Kozawa, S. Tagawa: International Congress of Radiation Research.

Dependence of Absorption Coefficient and Acid Generation Efficiency on Acid Generator Concentration in Chemically Amplified EUV Resist (poster), R. Hirose, \*T. Kozawa, S. Tagawa, T. Kai, T. Shimokawa: Microprocess and Nanotechnology Conference.

Effect of Fluorine Atom on Acid Generation in Chemically Amplified EUV Resists (poster), \*H. Yamamoto, T. Kozawa, S. Tagawa, H. Yukawa, M. Sato, J. Onodera: Microprocess and Nanotechnology Conference.

Study on the Reaction of Acid Generators with Epithermal Electrons (poster), K. Natsuda, T. Kozawa, A. Saeki, S. Tagawa, T. Kai, T. Shimokawa: Microprocess and Nanotechnology Conference.

Polymer nanowire formation along single particle tracks (poster): International Congress of Radiation Research.

Study on Dynamics of Radical Ions of Polystyrenes by Pulse Radiolysis (poster), \*K. Okamoto, M. Tanaka, T. Kozawa, S. Seki, S. Tagawa: International Congress of

Radiation Research.

Dynamics of Chemical Intermediates in CARs of Post-optical Lithographies (poster),  
\*A. Saeki: EUVL Symposium.

Pico- and subpico-second pulse radiolysis based on L-band linac with femtosecond white light continuum (poster), \*A. Saeki, T. Kozawa, S. Tagawa: ASR symposium.

### **Publications in Domestic Meetings**

|                                          |           |
|------------------------------------------|-----------|
| The Japan Society of Radiation Chemistry | 10 papers |
| The Japan Radiation Research Society     | 2 papers  |
| The Japan Society of Applied Physics:    | 12 papers |
| The Japan Society of Chemistry           | 2 papers  |
| The Japan Society of Polymer             | 2 papers  |

### **Academic Degrees**

#### **Doctor Degree for Engineering**

|             |                                                                                                             |
|-------------|-------------------------------------------------------------------------------------------------------------|
| Y. Koizumi  | Charge Carrier and Structural Dynamics of Designed Conjugated Oligomers                                     |
| H. Yamamoto | Resist Design for Next-Generation Lithography Based on Reaction Induced by Ionizing Radiation in Thin Films |

#### **Master Degree for Engineering**

|           |                                                                                                                                 |
|-----------|---------------------------------------------------------------------------------------------------------------------------------|
| R. Hirose | Dependence of Absorption Coefficient and Acid Generation Efficiency on Molecular Structures of Chemically Amplified EUV Resists |
|-----------|---------------------------------------------------------------------------------------------------------------------------------|

### **Sponsorships**

#### **Grant-in-Aid for Scientific Research on Priority Areas**

|           |                                                                                                        |             |
|-----------|--------------------------------------------------------------------------------------------------------|-------------|
| S. Tagawa | Femtosecond Pulse Radiolysis Study on Time Profile of Radiation-Induced Processes in Nanoscopic Region | ¥19,600,000 |
|-----------|--------------------------------------------------------------------------------------------------------|-------------|

#### **Grant-in-Aid for Young Scientists (A)**

|         |                                                                                                       |            |
|---------|-------------------------------------------------------------------------------------------------------|------------|
| S. Seki | Formation and characterization of nano-structures generated via chemical reactions by single ion beam | ¥3,300,000 |
|---------|-------------------------------------------------------------------------------------------------------|------------|

#### **Grant-in-Aid for Special Purposes**

|         |                                                                                                                              |            |
|---------|------------------------------------------------------------------------------------------------------------------------------|------------|
| S. Seki | Electrode-less evaluation of one-dimensional electric conductivity of single conjugated polymer chain by microwave technique | ¥1,400,000 |
|---------|------------------------------------------------------------------------------------------------------------------------------|------------|

#### **Grant-in-Aid for Scientific Research(C)**

|              |                                          |            |
|--------------|------------------------------------------|------------|
| K. Kobayashi | Mechanism in Regulation of Transcription | ¥2,200,000 |
|--------------|------------------------------------------|------------|

Factor containing Fe-S Clusters Sensing  
Oxidative Stress

**Grant-in-Aid for JSPS Fellows**

|             |                                                                                             |            |
|-------------|---------------------------------------------------------------------------------------------|------------|
| H. Yamamoto | Creation of novel lithographic process based on nano-beam-induced reaction mechanisms       | ¥900,000   |
| Y. Koizumi  | Contact-less evaluation of intrinsic conductive property of single conjugated polymer chain | ¥900,000   |
| R. Yamagami | Contact-less evaluation of intrinsic conductive property of single DNA molecule             | ¥1,000,000 |

**Entrusted Research**

|           |           |                                                                                                                   |             |
|-----------|-----------|-------------------------------------------------------------------------------------------------------------------|-------------|
| S. Tagawa | JST CREST | Research on resist for ultrafine fabrication and development of process simulator                                 | ¥26,910,000 |
| S. Tagawa | ASET      | Research on reaction mechanism of chemically amplified resist                                                     | ¥1,000,000  |
| S. Seki   | INSS      | Elucidation of degradation process of polymer upon exposure to radiation studied by microwave detection technique | ¥2,683,000  |

**Other Research Fund**

|           |                                 |                                 |          |
|-----------|---------------------------------|---------------------------------|----------|
| S. Tagawa | Mitsubishi gas chemical company | Basic study on ArF photo resist | ¥500,000 |
| S. Tagawa | SELETE                          | Research on EUV resists         | ¥500,000 |

# **Division of Next Industry Generation**

## **Outline**

Three new research departments have been established. The goal of each department is to provide advances in science and technology via close relationships with industry, which will lead to create a novel industry in the 21st century.

The departments are:

-Department of New Industry Projection

Perform research on new projects that can lead to industrial-structure innovations in the next generation.

-Department of New Industry Generation System(s)

Investigate and develop novel business systems that enable transfer of academic research outcomes to a new industry effectively and promptly, and that intend to improve productivity through responding to social demands.

-Department of Intellectual Property Research

Perform the strategic world-leading study of intellectual property linked with potential needs of the society, where the academia is required to create intellectual properties efficiently from the wide-ranging knowledge accumulated from academic research of the new interdisciplinary fields of material, information, and biology.

## **Achievement**

- The growth dynamics of Japanese firms classified in capital
- Development of a new intellectual property map
- Empirical study of effective creation and analysis of intellectual property
- Surveillance study of nanotechnology patents
- Entrusted surveillance study of thermoelectric materials for electric power generation

## Department of New Industrial Projection

Professor: Hiroshi KATAYAMA-YOSHIDA  
Designated Research Assoc.: Makoto NAKAZAWA  
Supporting Staff: Mika ASADA, Ryoko ITO

### Outline

Now in the 21st century, Japanese industrial structure is being transformed from a traditional industrial society to a knowledge-based society. In the knowledge-based society, instead of process innovation ("how to make"), product innovation ("what to make") is required. Thus new strategy for the change of the industrial structure is needed. We aim for the establishment of a framework to project new industries in future society (including the projection of the basic research required in the society) based on the analysis of the existing industries.

### Current Research Projects

#### **The growth dynamics of Japanese firms classified in capital**

We studied the distribution of size and growth rate of Japanese firms in 2005-2006. Under the commercial law of Japan, the firms are classified into three groups according to capital: big, middle-sized and small companies. By employing exhaustive lists of high-sales firms in Japan, we showed that the growth rates of profit for the groups were largely different in contrast to that of sales and increased in the order of capital from small to big. The result indicates that capital can be an important index to discuss the growth dynamics of the firms.

#### **Development of Intellectual Property Map**

The method for visualizing technology and market can be a very powerful tool to project new industries. To this end, we have developed an intellectual property map created by mapping both patent descriptions of interest and the keywords selected from the patent descriptions at the calculated position in the same plane. In this fiscal year, a beta version program to create the intellectual property map was implemented.

### Publications

#### **Publications in Domestic Meetings**

|                                           |         |
|-------------------------------------------|---------|
| The Physical Society of Japan             | 1 paper |
| Japan Society for Intellectual Production | 1 paper |

## **Department of Next Industry Generation Systems**

Specially Appointed Professor: Mototaka Senda, Ph.D.

### **Outline**

This Department was initiated from October, 2006 under the Division of Next Industry Generation including Department of New Industry Projection and Department of Intellectual Property Research, which will lead to create a novel industry in the 21<sup>st</sup> century. The Department focuses on investigation and development of novel business systems that enable transfer of academic research outcomes to a new industry effectively and promptly, and that intend to improve productivity through responding to social demands.

### **Current Research Projects**

- Functional Think Tank for Ideas, Technologies, Intellectual Properties and Business Opportunities in the University -

1. Discussion Group for the Future Drug Concept (New Drug Generation Business from Academic Seeds)
2. Discussion Group for the New Era of Life Science Research, Business, and Industry (New Interdisciplinary Fields Generation)
3. Research for Management of Intellectual Property and Technology (New Methodology for Intellectual Property Generation)
4. Science & Business Club (New Relationship between Academia and Industry)

Research fund (¥6,000,000 yen) was provided by ATECT Corporation, Ltd (Osaka) to this department.

- In order to perform a practical subject in the process of new industry generation systems, a few projects were installed and performed with collaboration of two laboratories in ISIR. Prof. Hiroyuki Noji (Department of Single Molecular Biophysics) and Associate Professor Takeshi Saito (Materials Science & Technology Research Center for Industrial Creation) have appointed to collaborate with ATECT Corporation and our department with appropriate selected projects.

## Department of Intellectual Property Research

Specially Appointed Professor: Hirokazu SHIMIZU

### Outlines

The object of this department is to perform the strategic world-leading study of intellectual property linked with potential needs of the society, where the academia is required to create intellectual properties efficiently from the wide-ranging knowledge accumulated from academic research of the new interdisciplinary fields of material, information, and biology.

### Current Research Project

#### Intellectual Property Engineering

Engineering method is studied to put intellectual properties of scientific knowledge to definite expression of patents and also to make detailed analysis and evaluation of published patents. This study has been made in collaboration with Human Interface Research Group of Materials Science & Technology Research Center for Industrial Creation.

#### Surveillance study of nanotechnology patents

Surveillance research of global nanotechnology patents was conducted to create new intellectual properties and industrial application of intellectual properties of academia.

#### Surveillance study of thermoelectric materials for electric power generation

The state of research and development of thermoelectric materials was investigated for feasibility study of thermoelectric power generation modules. This program was carried out as part of the feasibility study of thermoelectric power generation modules attachable for hot drain pipes under a grant from New Energy and Industrial Technology Development Organization.

### Sponsorship

#### Entrusted Research

|            |                         |                                                                                                                                                 |            |
|------------|-------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| H. Shimizu | Asset-Wits Co.,<br>ltd. | Surveillance research of<br>thermoelectric materials and<br>their electronic packaging<br>technologies for electric<br>power generation devices | ¥1,000,000 |
|------------|-------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|------------|

# **Activities of Centers**



## **Nanoscience and Nanotechnology Center**

Director Professor: Katsuaki SUGANUMA  
Support Staff: Mayo HAYASHI

### **Outline**

Nanoscience and Nanotechnology Center has passed the turning point of the nanotechnology mission for ten years. This center was founded in April 2002 for developing the Bottom-up Nanotechnology, the Top-down Nanotechnology, and their Industrial Applications in various fields. This center consists of four divisions; (1) Nanomaterial and Nanodevices, (2) Beam Science for Nanotechnology, (3) Nanoscience and Nanotechnology for Industrial Applications and (4) Nanocharacterization together with five laboratories (Radiation Laboratory, Electron Microscope Laboratory, Electronic Processing Laboratory, Nanofabrication Shop and Open Laboratory) and Nanotechnology Process Foundry. Each divisions and laboratories are quite active on the wide aspects of the nanotechnology area.

# Division of Nanomaterials and Nanodevices

## Outline

The main purpose of this division is to construct function harmonized nano-materials which can mimic flexible data processing like human body. By using typical “Bottom-up Nanotechnology” of artificial lattice technique, we combine metal, inorganic and (bio)organic materials at an atomic/molecular level to new nano-materials. The object of this division is also to research molecular-scale devices based on the function of single molecule. We are developing new techniques for the measurement of physical and chemical properties of single or several molecules. Furthermore, design and syntheses of supramolecules such as artificial DNA, proteins, photosynthetic molecules, and nanoparticles having more efficient and selective functions than those of single molecules are being investigated towards constructions of organized supramolecular systems such as artificial living cells and nano-devices exhibiting multifunction, complex properties, and conjugated functions. Proteins and their complexes with other biomolecules are regarded as nano bio devices. The research of our group is focused on structural and functional studies on such devices. We are also interested in developing highly sensitive biosensors and nano machines.

## Achievement

- Construction of functional nano-materials, which can mimic flexible data processing like human body.
- Investigation of relationship with structure and material properties at nano-scale.
- Development of bottom-up nanotechnology and control of nano-scale interface.
- Fusion of Bottom-up and Top-down Nanotechnologies
- Creation of super-five senses sensor and brain type memory.
- Programmed self-assembly and self-organization for molecular device.
- Control of electrode-molecule interface for molecular devices.
- Fabrication of top-contact nanoelectrode by nanoscale transfer-printing.
- Development of electrostatic force microscopy for insulating substrates.
- Methodological development of time-resolved electrostatic force detection.
- Electric property measurement of molecular interface and networks by point-contact current-imaging atomic force microscopy.
- Molecular recognition imaging by frequency modulation atomic force microscopy.
- Charge separation in DNA.
- Mechanism of photosensitized one-electron oxidation of DNA.
- Development of a novel branched polythiophene as an organic electronics material.
- Structural analysis of reaction intermediates formed on the catalytic cycle of copper amine oxidase.
- Purification and crystallization of MFS-type bacterial drug exporter.

# **Department of Artificial Nanomaterials for Bio-Information Systems**

Professor: Hidekazu TANAKA (2008.1.16-)  
Supporting Staff: Yumi NAGAI, Megumi IKEDA

## **Outlines**

The purpose of this research group is to create multi-function-harmonized nano-materials/devices which can mimic flexible information processing and memories such as a bio-system by using two processes of “Bottom-up” and “Top-down” nanotechnologies. Especially, we focus on functional oxide materials and try to develop a nano-fabrication technique combining bottom-up process by artificial lattice-fabrication using a pulsed laser deposition method and top-down process by nanoimprint and/or atomic force microscopy (AFM) lithography methods. Our fruition in the near future will lead creation of novel sensors, which are very sensitive to external information including light, temperature, electric and magnetic fields, and brain-mimic memories using magnetic spins. The main subject in this year are (1) Development of nano-patterning technique for exotic functional materials toward combination of Bottom-up and Top-down nanotechnologies, (2) Evaluation of physical properties in spinel ferrite thin films toward creation of novel functional devices, and (3) Fabrication of a magnetic field-effect-transistor using a heterostructure of ferroelectric gate / ferromagnetic channel layers.

## **Current Research Project**

### **Development of nano-patterning technique for exotic functional materials toward combination of Bottom-up and Top-down nanotechnologies**

The advance of nano-patterning techniques for functional oxide materials is an important subject toward not only construction of nano-integrated devices but also interest in nano-physics such as quantum effects. In the present situation, nano-fabrication techniques for oxide materials are not enough and the typical size of oxide devices are about several to hundreds micrometer orders by using photolithography. Meanwhile, we have established a nano-patterning technique at sub-50nm size so far using atomic force microscopy (AFM) lithography. Recently, as another promising method for oxide nano-patterning, we note a nanoimprint technique in order to produce nano-patterned structures with a large area.

Device makers in the field of Si processing expect this technique as a future manufacturing method with a low cost. If we can apply this technique to the oxide nanofabrication process, it would be an effective tool to fabricate oxide nanopatterns with a large area. However, typical organic resist masks are not feasible because high temperature process over several hundreds degree Celsius include to form epitaxial oxide films. Here in our group, the Mo masks were used as the heat-enduring resist, having stable performance even at high temperature, instead of polymer resists. We show a nanoimprint process performed for spinel ferrite (Fe,Mn)<sub>3</sub>O<sub>4</sub> (FMO) thin films

as a example; (i) The Mo resist was sputtered on the PMMA layer patterned by nanoimprint on an  $\text{Al}_2\text{O}_3(0001)$  substrate (2cm x 2cm). (ii) The PMMA resist was removed by dissolving in acetone solvent and only the Mo nano-mask patterned remains. (iii) The FMO film was epitaxially deposited on this mask by a PLD technique under the condition of 360 degree for substrate-temperature and  $10^{-4}$  Pa for oxygen-pressure. At that time the Mo nano-patterned resist endured against such a high temperature-fabrication-process. (iv) The Mo layer was removed by ultrasonication in  $\text{H}_2\text{O}_2$  solvent. Finally, the FMO nano-pattern was formed.

Thus we successfully obtained nano-dot array of 100 nm size with a large area in epitaxial FMO films.

### **Evaluation of physical properties in spinel ferrite thin films toward creation of novel functional devices**

Fe-based oxides with spinel structures exhibit ferrimagnetism with a very high Curie temperature ( $T_C$ ), which are used industrially for recoding media. The general electric properties are insulating. Only a few conductive spinel oxides such as  $\text{Fe}_3\text{O}_4$  are expected as half-metals and represent promising characters as room-temperature spintronic devices. However, these conducting spinel oxides have a huge carrier concentration ( $10^{22}/\text{cm}^3$ ), which cannot be available to control in carriers such a semiconductor technology. That is why research for tunable ferromagnetic semiconductor oxides would be desirable to realize oxide spintronics applications working at high temperature above room temperature. Here we propose that the solid solution system of  $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$  (FZO) with high  $T_C$  should be possibly the best candidate in regard to tunability of carrier concentration, and evaluated the physical properties of the thin films fabricated by a PLD technique. The electrical conductivity and magnetic properties of FZO thin films were systematically modulated for the entire range of Zn substitution. Anomalous Hall coefficient measurements revealed the presence of spin-polarized carriers at room temperature. Valence band spectra obtained by hard x-ray photoemission spectroscopy revealed that the density of states near the Fermi level was reduced with increasing Zn concentration of  $x$ . These results indicate that this system will serve as a tunable ferromagnetic semiconductor with a strong electron correlation.

The findings of this investigation suggest that this material holds great promise for the development of advanced spin electronics working at room temperature.

### **Fabrication of a magnetic field-effect-transistor using a heterostructure of ferroelectric gate / ferromagnetic channel layers**

$\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$  (FZO) thin films show semiconductive behavior with high spin polarization and high  $T_C$  over 400 K as mentioned above and have enough potential for applying novel functional applications.

As a demonstration for new applications, we fabricated ferromagnetic-FET of FZO channel/ferroelectric  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  gate hetero-junction and evaluated their magnetic and electrical properties. We verified modulation of magnetic coercivity and conductivity in the magnetic channel by polarization reverse of the ferroelectric gate at room temperature. This result suggests that strong coupling between magnetism and conductivity exists through the double exchange interaction even at room temperature, which can extend possibility of device-functionality. Thus spinel ferrite materials such a

FZO have enough potential for oxide spin functional electronics working high temperature.

## **Publications**

### **Original Papers**

Electronic structures of  $\text{Fe}_{3-x}\text{M}_x\text{O}_4$  ( $M=\text{Mn}, \text{Zn}$ ) spinel oxide thin films investigated by x-ray photoemission spectroscopy and x-ray magnetic circular dichroism, J. Takaobushi, M. Ishikawa, S. Ueda, E. Ikenaga, J.-J. Kim, M. Kobata, Y. Takeda, Y. Saitoh, M. Yabashi, Y. Nishino, D. Miwa, K. Tamasaku, T. Ishikawa, I. Satoh, H. Tanaka, K. Kobayashi, T. Kawai: Phys. Rev. B, 76 (2007) 205108.

Interface Effect on Metal-Insulator Transition of Strained Vanadium Dioxide Ultrathin Films, K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai: J. Appl. Phys., 101 (2007) 026103.

Thickness Dependence of Structure and Magnetization of  $\text{BiFeO}_3$  Films on  $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$  (001) Substrate, D.S. Rana, K. Takahashi, K.R. Mavani, I. Kawayama, H. Murakami, M. Tonouchi, T. Yanagida, H. Tanaka and T. Kawai: Phys. Rev. B, 75 (2007) 060405.

Functional lipid vesicles based on artificial electric-taster sensor, H.S. Jung, H. Tanaka, H.Y. Lee, T. Kawai: Molecular Crystals and Liquid Crystals, 463 (2007) 553-561.

Control of Magnesium Oxide Nanowire Morphologies by Ambient Temperature, K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai: Appl. Phys. Lett., 90 (2007) 233103.

Epitaxial growth of MgO nanowires by pulsed laser deposition, K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai: J. Appl. Phys., 101 (2007) 124304.

Effect of ablated particle flux on MgO nanowire growth by pulsed laser deposition, A. Marcu, T. Yanagida, K. Nagashima, H. Tanaka, and T. Kawai: J. Appl. Phys., 102 (2007) 016102.

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Transport properties of  $\text{ZnFe}_2\text{O}_4$ -delta thin films, A. Marcu, T. Yanagida, K. Nagashima, H. Tanaka and T. Kawai: J. Appl. Phys., 102 (2007) 023713.

Mechanism of catalyst diffusion on magnesium oxide nanowire growth, T. Yanagida, K. Nagashima, H. Tanaka, T. Kawai: Appl. Phys. Lett., 91 (2007) 061502.

Epitaxial transition metal oxide nanostructures fabricated by a combination of AFM lithography and molybdenum lift-off, N. Suzuki, H. Tanaka, T. Kawai: Advanced Materials, 20 (2008) 909-913.

Development of a Design Supporting System for Nano-Materials based on a Framework for Integrated Knowledge of Functioning-Manufacturing Process, S. Tarumi, K. Kozaki, Y. Kitamura, H. Tanaka and R. Mizoguchi: Transactions of the Japanese Soc. for Artificial Intelligence, 23 (1) (2008) 36-49.

### **Review Papers**

Nano Fabrication of Functional Transition Metal Oxide Thin Film, H. Tanaka, T. Kanki, J. Takaobushi, and T. Kawai: J. Vac. Soc. Jpn., vol. 51 (2008) 37-43.

Spintronics Device Based on Heterostructured Strongly Correlated Oxides, H. Tanaka, T. Kanki, J. Takaobushi, and T. Kawai: Function & Materials, vol. 28 (2008) 54-62.

### **Patents**

Non-Volatile Photon Memory and their Wiring and Reading Method, T. Kawai, H. Tanaka, Y.G. Park, H.Y Lee, and T. Kanki, Patent No.3972096

Preparation of Low Resistive  $\text{SrTiO}_3$ , H. Katayama-Yoshida, K. Betsuyaku, T. Kawai, and H. Tanaka, Patent No. 4004205

Patterning Method and their Resulting Layered Structures, Arrayed Substrates, Electric Devices, T. Kawai, H. Tanaka, and N. Suzuki, Tokkai2008-053473

Tunneling Magnetoresistance Device Semiconductor Junction Device Magnetic Memory and Semiconductor Light-Emitting Device, H. Tanaka, and T. Kawai, Patent No. US7309903 B2 (USA)

Field-Effect Transistor, H. Tanaka, T. Kanki, Y.G. Park, and T. Kawai, Patent No. 10-0731960 (Korea)

### **International Conferences**

Construction of Ferromagnetic Oxides Nano-Channel Structures Toward Nano area-FET devices by AFM Lithography (invited), \*H. Tanaka, T. Kawai: 2007 Materials Research Society Spring Meeting, San Francisco, USA, April 9-14, 2007.

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Nanowire Heterostructures of Transition Metal Oxides (poster), \*T. Yanagida, K. Nagashima, A. Marcu, H. Tanaka and T. Kawai: The 14th International Workshop on Oxide Electronics, Jeju island, Korea, October 7-10, 2007.

Large-area nano patterning of transition metal oxide films by the nanoimprint lithography based Mo lift-off technique (poster), \*N. Suzuki, S. Yamanaka, H. Tanaka,

B. K. Lee, H. Y. Lee and T. Kawai: The 14th International Workshop on Oxide Electronics, Jeju island, Korea, October 7-10, 2007.

Electric Field Modulation of Magnetism in Spinel Ferrite Field Effect Transistor at Room Temperature (poster), \*J. Takaobushi, H. Tanaka, T. Kawai: 1st Global COE International Symposium Electronic Devices Innovation (EDIS 2008), Osaka, Japan, January 21-22, 2008.

Fabrication of  $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$  nanostructure using Mo nanomask AFM lithography (poster), \*K. goto, H. Tanaka, T. Kawai: 1st Global COE International Symposium Electronic Devices Innovation (EDIS 2008), Osaka, Japan, January 21-22, 2008.

High throughput fabrication of the integrated  $\text{Fe}_{3-x}\text{M}_x\text{O}_4$  (M=Mn and Zn) nano array structures in large area by Nanoimprint lithography with Mo lift-off technique and their magnetic properties (poster), \*S. Yamanaka, N. Suzuki, B. K. Lee, H. Y. Lee, H. Tanaka, T. Kawai: 1st Global COE International Symposium Electronic Devices Innovation (EDIS 2008), Osaka, Japan, January 21-22, 2008.

Significance of 3D Epitaxy on Heterostructured Oxide Nanowires (poster), \*K. Oka, T. Yanagida, K. Nagashima, H. Tanaka, and T. Kawai: 1st Global COE International Symposium Electronic Devices Innovation (EDIS 2008), Osaka, Japan, January 21-22, 2008.

Crucial role of heterointerface on MgO/titanate core-shell nanowires (poster), \*K. Nagashima, T. Yanagida, K. Oka, H. Tanaka, S. Seki, A. Saeki, S. Tagawa and T. Kawai: 1st Global COE International Symposium Electronic Devices Innovation (EDIS 2008), Osaka, Japan, January 21-22, 2008.

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Fabrication of  $(\text{Fe,Mn})_3\text{O}_4$  nanostructure using Mo nanomask AFM lithography (poster), \*K. goto, H. Tanaka, T. Kawai: 11th Sanken, 6th Nanotechnology Center and 1st MSTEC International Symposium New Advances in Nanoscience & Nanotechnology, Hyogo, Japan, February 4-5, 2008.

High throughput fabrication of the integrated  $\text{Fe}_{3-x}\text{M}_x\text{O}_4$  (M=Mn and Zn) nano array structures in large area by Nanoimprint lithography with Mo lift-off technique and their magnetic properties (poster), \*S. Yamanaka, N. Suzuki, B. K. Lee, H. Y. Lee, H. Tanaka, T. Kawai: 11th Sanken, 6th Nanotechnology Center and 1st MSTEC International Symposium New Advances in Nanoscience & Nanotechnology, Hyogo, Japan, February 4-5, 2008.

Crucial role of Heterointerface on Transport Properties of In-situ Formed MgO/titanate Core-shell Nanowires (poster), \*K. Oka, K. Nagashima, T. Yanagida, H. Tanaka, T. Kawai, S. Seki, A. Saeki and S. Tagawa: 11th Sanken, 6th Nanotechnology Center and

1st MSTEC International Symposium New Advances in Nanoscience & Nanotechnology, Hyogo, Japan, February 4-5, 2008.

Transport Nature of Low Temperature Grown NiO Thin Films (poster), \*K. Oka, T. Yanagida, K. Nagashima, H. Tanaka, and T. Kawai: 11th Sanken, 6th Nanotechnology Center and 1st MSTEC International Symposium New Advances in Nanoscience & Nanotechnology, Hyogo, Japan, February 4-5, 2008.

In-situ Formation of MgO/NiO Heterostructured Oxide Nanowires (poster), \*K. Oka, T. Yanagida, K. Nagashima, H. Tanaka and T. Kawai: 11th Sanken, 6th Nanotechnology Center and 1st MSTEC International Symposium New Advances in Nanoscience & Nanotechnology, Hyogo, Japan, February 4-5, 2008.

Effect of Heterointerface on Transport Properties of In-situ Formed MgO/titanate Core-shell Nanowires (poster), \*K. Oka, K. Nagashima, T. Yanagida, H. Tanaka and T. Kawai: 15th International Colloquim on Scanning Probe Microscopy (ICPM15), Shizuoka, Japan, December 6-8, 2007.

Role of Theree-Dimensional Epitaxy on MgO/NiO Heterostructured Oxide Nanowire Formation (poster), \*K. Oka, K. Nagashima, T. Yanagida, H. Tanaka and T. Kawai: 15th International Colloquim on Scanning Probe Microscopy (ICPM15), Shizuoka, Japan, December 6-8, 2007.

Nature of Transport Properties in Low Temperature Grown NiO Films (poster), \*K. Oka, K. Nagashima, T. Yanagida, H. Tanaka and T. Kawai: 15th International Colloquim on Scanning Probe Microscopy (ICPM15), Shizuoka, Japan, December 6-8, 2007.

Development of a Design Supporting System for Nano-Materials based on a Framework for Integrated Knowledge of Functioning-Manufacturing Process, \*S. Tarumi, K. Kozaki, Y. Kitamura, H. Tanaka and R. Mizoguchi: The 10th IASTED International Conference Intelligent Systems and Control(ISC2007),Cambridge, Massachusetts, USA, Novemb 19-21, 2007.

#### **Contributions to International Conferences and Journals**

|           |                                                                                                  |
|-----------|--------------------------------------------------------------------------------------------------|
| H. Tanaka | The IEEE Nanotechnology Materials and Device Conference (NMDC 2008) (Sub-Committee Member)       |
| H. Tanaka | 4th Handai Nano Science and Nanotechnology International Symposium (Organizing Committee. Chair) |

#### **Publications in Domestic Meetings**

|                                      |         |
|--------------------------------------|---------|
| The Vacuum Society of Japan          | 1 paper |
| The Physical Society of Japan        | 1 paper |
| The Japan Society of Applied Physics | 1 paper |

#### **Sponsorship**



**Grant-in-Aid for Scientific Research on Exploratory Research**

|           |                                                                                 |            |
|-----------|---------------------------------------------------------------------------------|------------|
| H. Tanaka | Development of 3 Dimensional Epitaxy<br>Technique by Nano-particle via Solution | ¥1,300,000 |
|-----------|---------------------------------------------------------------------------------|------------|

**Entrusted Research**

|           |                                                                   |                                                                                                          |            |
|-----------|-------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|------------|
| H. Tanaka | JASRI/SPRING-8,<br>National Institute<br>for Materials<br>Science | Development of Hard<br>X-ray Photoemission<br>Microscope for 3<br>Dimensional Chemical<br>State Analysis | ¥1,712,269 |
|-----------|-------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|------------|

**Other Research Fund**

|           |                                                        |          |
|-----------|--------------------------------------------------------|----------|
| H. Tanaka | The Mikiya Science and Technology Foundation           | ¥820,000 |
| H. Tanaka | Kansai Research Foundation for Technology<br>Promotion | ¥80,000  |

## Department of Single-Molecular Integrated Devices

|                                          |                  |
|------------------------------------------|------------------|
| Professor:                               | Tomoji KAWAI     |
| Associate Professor:                     | Takuya MATSUMOTO |
| Specially Appointed Research Associates: | Bong-Kuk LEE     |
| Support Staff:                           | Yumiko NOGI      |

### Outlines

Notwithstanding the great anticipation of the potential of molecular-scale electronics, it is very difficult to fabricate molecular-devices, owing to the lack of effective technologies for wiring molecules and connecting molecules to electrode. Self-organization is a promising route to fabricating complicated nanostructure by “bottom-up” process with highly selective chemical-reactions.

The object of this department is to research molecular-scale devices and electrochemical nanobiosensor system based on the function of single molecule. We are developing new techniques for the measurement of electrical properties for molecular nanostructures. We are also developing an interconnect method to program three kinds of component molecules with their own functions, and to create a molecular device between nano-scale electrodes in a self-organized manner. For biosensor, it is necessary to establish the elemental technologies, such as a nanopatterning of substrate using a top-down technique, the self-assembled nanoarray of probe biomolecule into the nanostructured substrate using a bottom-up technique, and the detection of the target biomolecules using an electrochemical technique.

### Current Research Project

#### Metallic Nature of Metal–Molecule Interface Formed by Au–Se Bonds

Although Au–S bonds have been widely used as the bonds for creating conventional metal–molecule interfaces, self-assembled films formed using this bond can exist in several structures, which prevents the formation of a uniform structure over a wide range. Furthermore, Au–S bonds have a high charge injection barrier from the electrode to the molecule, which is a drawback for molecular devices. In this research, we determined the structure and electronic states of the metal–molecule interface formed by Au–Se bonds, and found that the interface is a useful metal–molecule interface from the viewpoint of molecular devices. These results indicate that metal–molecule interfaces formed by Au–Se bonds have high potential for improving the properties of molecular devices that are currently being developed, such as organic field-effect transistors, organic electroluminescence devices, biochips, and nanoscale molecular devices.

#### Formation and Self-Breaking Mechanism of Stable Atom-Sized Junctions

Forming a stable single molecule junction is a prerequisite for realization of molecular electronics, which is in general a formidable task to achieve. Despite the significance, it is yet to be clarified to what extent mechanical perturbations, a common source of destabilization, affects the junction stability. The study addresses this issue by investigating intrinsic thermodynamic stability and breakdown characteristics of the

single atom contacts through systematic measurements of the stretching rate dependence of the junction lifetime. It provides solid evidence suggesting critical importance of device systems with mechanical stability of better than picometer range to fabricate stable atomic/molecular-scale junctions by experimentally realizing unprecedented single atom/molecule junction life time. The outstanding mechanical stability of the nano-fabricated mechanically controllable break junction establishes an ideal experimental platform to study electron transport in single molecules by realizing unprecedented long-time holding of single molecule junctions, about 10000 times more potent than the conventional techniques such as SPM break junctions.

### **Electrostatic force microscopy of nano-scale structure on insulating substrates**

Imaging of local charges on insulating substrate play important roles for the studies of nano-scale electronic devices. We found that potential and capacitance images of nano-scale adsorbates on *insulating* substrates can be obtained by frequency-mode surface potential microscopy. This finding is beyond the common understanding based on a parallel-plate capacitor model because the charges of nano-structure on insulating substrate should be almost negligible in comparison with that of bulk substrate. We calculated spatial distributions of the electric field just below a sharp tip apex using finite element method. The results show that the electric potential at the substrate surface remains ca. 10 % of the bias voltage applied to the electrode contacting with backside of the substrate. This potential is influenced by variation of tip-surface distance because, in essential, the surface potential is partial voltage divided with tip-surface space and substrate thickness. However, in case of sharp tip, the surface potential is mainly governed by field gradients in the subsurface of substrate and in the space surrounding tip-surface gap. As a result, the variation range of surface potential is only 5-15 % with the change of tip-surface distance from 0.1 to 3 nm. In the basis of this calculation, we obtained absolute dipole moments of double-stranded DNA, Au-nanoparticles (AuNP) coated with citric acid, and transcription complex (protein) on mica substrates from surface potential images of these nanoscale materials. The values of DNA, AuNP, and protein are 0.08 D/nm<sup>2</sup>, 0.05 D/particle and 0.004 D/molecule, respectively. These results demonstrate that surface potential microscopy provide comparable result with the measurement at conductive surface and scanning tunneling microscopy.

## **Publications**

### **Original Papers**

Anchoring Gold Nanoparticles Onto a Mica Surface by Oxygen Plasma Ashing for Sequential Nanocomponent Assembly, A. Takagi, K. Ojima, E. Mikamo, T. Matsumoto and T. Kawai: Appl. Phys. Lett., 90 (4) (2007) 043122-1-04312-3.

Refinement of Conditions of Point-contact Current Imaging Atomic Force Microscopy for Molecular-Scale Conduction Measurements, T. Yajima, H. Tanaka, T. Matsumoto, Y. Otsuka, Y. Sugawara and T. Ogawa: Nanotechnology, 18 (9) (2007) 095501 (5pp).

Tunnelling Charge Injection into a Pentacene Layer Using Dynamic-Mode Scanning

Force Microscopy, T. Kusaka, K. Ojima, T. Matsumoto and T. Kawai: Nanotechnology, 18 (9) (2007) 095503 (5pp).

Discrete Dihedral-Angle Modulation in Porphyrin Wheels Adsorbed on Cu(100) Observed by Scanning Tunneling Microscopy, A. Takagi, T. Hori, X. Peng, N. Aratani, T. Matsumoto, A. Osuka and T. Kawai: Surface Sci., 601 (10) (2007) 2178-2181.

Control of the Electrode-Molecule Interface for Molecular Devices, K. Yokota, M. Taniguchi and T. Kawai: J. Am. Chem. Soc., 129 (18) (2007) 5818-5819.

Electronic States of The DNA Polynucleotides Poly(dG)poly(dC) in The Presence of Iodine, M. Furukawa, Hiroyuki S. Kato, M. Taniguchi, T. Kawai, T. Hatsui, N. Kosugi, T. Yoshida, M. Aida and M. Kawai: Phys. Rev. B, 75 (4) (2007) 045119-045127.

Synthesis of Dendritic Oligothiophenes and Their Self-Association Properties by Intermolecular - Interactions, N. Negishi, Y. Ie, M. Taniguchi, T. Kawai, H. Tada, T. Kaneda and Y Aso: Org. Lett., 9 (5) (2007) 829-832.

Infrared Spectroscopy on poly(dG)-Poly(dC) DNA at Low Hydration, H. Abdurakhman, K. Tajiri, H. Yokoi, N. Kuroda, H. Matsui, T. Yanagimachi, M. Taniguchi, T. Kawai and N. Toyota: J. Phys. Soc. Jpn., 76 (2) (2007) 024009-024014.

Synthesis of Nanometer-Scale Porphyrin Wheels of Variable Size, T. Hori, X. Peng, N. Aratani, A. Takagi, T. Matsumoto, T. Kawai, Z. S. Yoon, M.-C. Yoon, J. Yang, D. Kim, and A. Osuka: Chem. Eur. J., 14 (2) (2008) 582-595.

## **Review Papers**

Kansatsurei3-DNA ( in Japanese), Takuya Matsumoto, Hyomen-Buusei-Kogaku Handbook 2ed., p. 292-293, Section 2.3, Chapter 6 (2007)

Bunshi Manipureshon ( in Japanese), Takuya Matsumoto, Hyomen-Buusei-Kogaku Handbook 2ed., p. 769-772, Section 2, Chapter 19 (2007).

Development of Nano Molecular Devices Using Self-organized Interconnect Method, Masateru taniguchi, Tomoji Kawai, The Bulletin of the Nano Science and Technology 6 [1], (2007) 23-28

## **Patents**

Probe device, Takuya Matsumoto, Yasuhisa Naitoh, Tomoji Kawai, US 7,250,602 B2

Fine structure controll of nano-particle catalyst using nucleic acid, Yasushi maeda, Tadahiro Fugitani, Masataka Kouyama, Takuya Matsumoto, Akihiko Takagi, Tokugan 2007-296175

### International Conferences

Hopping Conduction Through Macromolecules (invited), \*T. Msatsumoto: The Nanoelectronics and Dynamics of DNA, Hawaii, U.S.A. Aug 26-28, 2007.

Self-organized interconnect method for molecular devices, \*M. Taniguchi, J. Terao, T. Kawai: Electron transport through a linked molecule in nano-scale, Tokyo, Japan, Aug 18-20, 2007.

Interface and Grain Boundary in Organic Nanoelectronics (invited), \*T. Msatsumoto: Printed Electronics ASIA07, Tokyo, Japan Sep 10-11, 2007.

Surface Potential and Capacitance Images of Biological Molecules on Insulating Substrates (poster), \*T. Matsumoto, F. Yamada, E. Mikamo-Sato, A. Takagi, T. Kawai: 10th International Non-Contact AFM 2007, Antalya, Turkey, Sep16-20, 2007.

Molecule Recognition Imaging by Frequency Shift Detection in Liquid, \*T. Matsumoto, T. Kawahara, H. Hokonohara, T. Kawai: 10th International Non-Contact AFM 2007, Antalya, Turkey, Sep16-20, 2007.

Nanoscale Hopping Conduction Through Cytochrome c and Mn12-complex (invited), \*T. Msatsumoto: Seminar at physics department of Genova University, Genova, Italy, Sep 24, 2007.

Surface Potential and Capacitance Images of Biological Molecules on Insulating Substrates, \*T. Matsumoto, F. Yamada, E. Mikamo-Sato, A. Takagi, T. Kawai: 15th International Colloquium on Scanning Probe Microscopy (ICSPM15), Atagawa, Japan, Dec. 6- 8, 2007.

Inelastic tunneling spectroscopy of single molecule using nanofabricated mechanically controllable break-junction (invited), M. Taniguchi, M. Tsutsui, K. Shoji, T. Kawai: CREST Symposium on Theories and Simulations for Charge Migration and Chemical Reactions at Nano-Scale Interfaces, Tsukuba, Japan, Jan 29-31, 2008.

### Contributions to International Conferences and Journals

|              |                                                                                            |
|--------------|--------------------------------------------------------------------------------------------|
| T. Matsumoto | International Symposium on Surface Science and Nanotechnology (ISSS-5) (Program Committee) |
| T. Matsumoto | e-Journal of Surface Science and Nanotechnology (Editorial Board)                          |

### Publications in Domestic Meetings

|                                             |          |
|---------------------------------------------|----------|
| The Japan Society of Applied Physics        | 18papers |
| The Physical Society of Japan               | 7papers  |
| Discussion meeting for molecular structures | 3papers  |
| The Chemical Society of Japan               | 3papers  |
| Others                                      | 6papers  |

## Academic Degrees

### Doctor Degree for Science

F.Yamada                      Studies on nanoscale electrical and magnetic properties of DNA complexes with nanoparticles and molecules

### Master Degree for Engineering Science

H.Kawaguchi                Influence of gate insulators on device characteristics of ambipolar organic field-effect transistors

## Sponsorship

### Grant-in-Aid for Young Scientists (B)

M. Taniguchi                Development of Self-Organized Molecular                      ¥500,000  
Devices

### Scientific Research in Priority Areas

M. Taniguchi                Development of Control Technique of                      ¥2,100,000  
Molecule-Electrode Interface

### Entrusted Research

M. Taniguchi                Japan Science and Technology Corporation                      Creation of Ultra-High Integrated Molecular devices Using Self-Organized Interconnect Method                      ¥3,198,000

### Cooperative Research

M. Taniguchi                Matsushita Electric Industrial Company                      Development of new functional materials based on pi-conjugated molecules covered with CD                      ¥2,250,000

### Other Research Fund

T. Matsumoto                Nippon Sheet Glass Foundation for Materials Science and Engineering                      Room temperature magnetoresistance of Nanoscale Mn12-complex array                      ¥1,450,000

T. Matsumoto                Iketani Science and Technology Foundation                      Room temperature magnetoresistance devices of self-organized nanoscale molecular array using DNA templates.                      ¥1,500,000

T. Matsumoto                The Foundation for                      Fabrication and evaluation of top-contact electrode and                      ¥1,000,000

|              |                                                        |                                            |            |
|--------------|--------------------------------------------------------|--------------------------------------------|------------|
|              | Technology<br>Promotion<br>Electronic Circuit<br>Board | of circuit using nano-transfer<br>printing |            |
| M. Taniguchi | Shin-Etsu<br>Chemical Co., Ltd                         | Development of FET                         | ¥2,000,000 |

## Department of Supramolecular Chemistry

Professor: Tetsuro MAJIMA  
Associate Professor: Kiyohiko KAWAI  
Research Associate: Shinobu TAKIZAWA, Makoto Karakawa

### Outlines

Towards the construction of organized supramolecular systems with multifunctionality, the design and syntheses of supramolecules such as spherical nanoparticles, artificial DNA, proteins, photosynthetic molecules, and metal-bridged polymers having more efficient and selective functions than those of single molecules have been investigated.

Asymmetric synthesis, a phenomenon fine tuned to perfection by nature, forms the central theme of our research efforts. We have been interested in the design and syntheses of a novel class of chiral nano-complexes that are unique in promoting new asymmetric reactions. The mechanisms of these organic reactions are also studied by means of physical organic techniques.

### Current Research Project

#### Charge Separation in DNA

The formation of the long-lived charge-separated state in DNA upon visible light irradiation is of particular interest in molecular-scale optoelectronics, sensor design, and other areas of nano-technology. However, the efficient generation of the charge-separated state is hampered by fast charge recombination within a contact ion-pair, which limits the application of DNA for photoelectrochemical sensors and devices. In this study, a series of protonated 9-alkylamino-6-chloro-2-methoxyacridine ( $\text{Acr}^+$ ) and phenothiazine (Ptz) modified DNAs were synthesized for the further understanding of the mechanism of charge separation in DNA in order to generate a long-lived charge-separated state with a high quantum yield ( $\Phi$ ). The  $\text{Acr}^+$  serves as a photosensitizer to produce a hole on guanine (G), and the G-C base-pairs were used as a hole transporting pathway to separate a hole from  $\text{Acr}^\bullet$  (the one-electron reduced form of  $\text{Acr}^+$ ) to be trapped at Ptz. Since  $\text{Acr}^+$  oxidizes only G upon photoexcitation, the A-T base-pair can be used as a spacer between  $\text{Acr}^+$  and the G-C base-pair to avoid the formation of a contact ion-pair. The charge injection dynamics was investigated by steady-state fluorescence spectra and fluorescence lifetime measurements, and the  $\Phi$  and the lifetime of the charge-separated state produced upon photoirradiation were assessed by nanosecond laser flash photolysis of the  $\text{Acr}^+$ - and Ptz-modified DNA. A long-lived charge-separated state was successfully formed upon visible-light irradiation and the  $\Phi$  was the highest for the DNA having a single intervening A-T base-pair between  $\text{Acr}^+$  and the G-C base pair. These results clearly demonstrated that the charge separation process in DNA can be refined by putting a redox inactive intervening base-pair as a spacer between a photosensitizer and the nucleobase to be oxidized to slow down the charge recombination rate.



### **Dinuclear Chiral Vanadium Catalysts for Oxidative Coupling of 2-Naphthols via a Dual Activation Mechanism**

The dinuclear vanadium(IV) complex was prepared by complexation of VOSO<sub>4</sub> with the Schiff base derived from (*R*)-3,3'-diformyl-2,2'-dihydroxy-1,1'-binaphthyl and (*S*)-*tert*-leucine. Since the dinuclear vanadium(IV) complex was found to be readily oxidized to afford a corresponding vanadium(V) species during preparation in air, a new synthetic procedure using VOCl<sub>3</sub> has been applied towards dinuclear vanadium(V) complexes. To the best of our knowledge, these dinuclear complexes show considerably higher catalytic activity than previously reported vanadium complexes for the oxidative coupling of 2-naphthols.

### **Development of a novel branched polythiophene as a organic electronics material.**

We have investigated an organic field-effect transistor (FET) of polymer materials focused on an intermolecular interaction in a polymer thin-film structure. Previously, it was reported that a branched oligothiophene showed a strong 3D intermolecular interaction in a solution. On the basis of the knowledge, we have designed and synthesis of a novel branched polythiophene constructed with a di-bromo-phenyl thiophene derivative and quarter thiophene units coupling by a stille-coupling method. GPC measurement results of the compounds show including a supramolecular weight fraction located adjacent to exclusion limit of a GPC column. Original molecular weight was also detected in a range of 8000-10000. The supramolecular weight fraction might be derived from an intermolecular interaction or assembly of branched-units of the polymers. Few of these polymers showed p-type FET characteristics. Further investigations about device fabrication with the polymers are in progress.

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### **Books**

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“Single-Molecule Fluorescence Imaging Techniques for the Detection of Reactive Oxygen Species”, “Modern Research and Educational Topics on Microscopy” (ed by A. Mendez-Vilas and J. Diaz), T. Tachikawa and T. Majima, Formatex, (2007) 651-659.

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“Single molecule fluorescence imaging in photocatalytic reaction”, in “New chemistry world by photon and interface: photocatalyst and photoenergy conversion”, T. Majima, Kuba-pro Co. (2008) 50-58.

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“Preparation of metal nanoparticles in matrices”, T. Majima, M. Sakamoto, M. Fujitsuka, No. 2007-28166.

“Preparation of modified metal nanoparticles and its method”, T. Majima, M. Sakamoto,

M. Fujitsuka, No. 2007-095031.

“polymers, a thin-film and organic electronics device using the polymer”, Y. Aso, M. Karakawa, M. Ueda, No. 2008-032021

### **International Conferences**

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Mechanistic Insight into the  $\text{TiO}_2$  Photocatalytic Reactions (invited), T. Majima: 23th International Conference on Photochemistry, Cologne, Germany, July 29-Aug. 3, 2007.

Rapid Energy Migration along Photofunctional Polymers (poster), M. Fujitsuka and \*T. Majima: 23th International Conference on Photochemistry, Cologne, Germany, July 29-Aug. 3, 2007.

Charge Separation via Rapid Hole Transfer through Adenine-Hopping (poster), T. Takada, K. Kawai, M. Fujitsuka, and \*T. Majima: 23th International Conference on Photochemistry, Cologne, Germany, July 29-Aug. 3, 2007.

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Photochemical synthesis of metal nanoparticles in a PVA film (invited), \*M. Sakamoto and T. Majima: Langmuir Symposium 2007 in Osaka University, Suita, Japan, Oct. 9, 2007.

Development of New  $\text{TiO}_2$  Photocatalysts (invited), T. Majima: 7th Pacific Rim Conference on Ceramic and Glass Technology, Shanghai, Nov. 11-14, 2007.

Adsorption and Electron Transfer Processes of Perylene Diimide Dye on  $\text{TiO}_2$  Nanoparticles Studied by Single-Molecule (poster), S.-C. Cui, T. Tachikawa, S. Tojo, M. Fujitsuka, T. Majima: 7th Pacific Rim Conference on Ceramic and Glass Technology, Shanghai, Nov. 11-14, 2007.

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Intramolecular Electron Transfer from Axial Ligands to  $\text{S}_2$ -Excited Tetraphenyl Porphyrins (invited), \*M. Fujitsuka and T. Majima: 2007 Korea-Japan Symposium on Frontier Photoscience, Gyeongju, Korea, Nov. 22-25, 2007.

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Development of New  $TiO_2$  Photocatalyst: Mechanistic Study of  $TiO_2$  Photocatalytic Reactions (invited), T. Majima: The 9th International Symposium on Eco-materials Processing and Design, Changwon Exhibition Convention Center, Changwon, Korea, Jan. 7-9, 2008.

Photoinduced Charge Separation in Titania Nanotubes (poster), \*T. Tachikawa, S. Tojo, M. Fujitsuka, T. Sekino, and T. Majima: The 9th International Symposium on Eco-materials Processing and Design, Changwon Exhibition Convention Center, Changwon, Korea, Jan. 7-9, 2008.

Single-Molecule Detection of Airborne Singlet Oxygen (poster), \*K. Naito, T. Tachikawa, S.-C. Cui, A. Sugimoto, M. Fujitsuka, and T. Majima: The 9th International Symposium on Eco-materials Processing and Design, Changwon Exhibition Convention Center, Changwon, Korea, Jan. 7-9, 2008.

Charge Separation in Acridine Modified DNA (poster), \*K. Kawai, M. Fujitsuka, and T. Majima: 11th Sanken International Symposium / 6th nanotechnology center international symposium / 1st MSTEC international symposium, Awaji, Japan, Feb. 4-5, 2008.

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Intramolecular Electron Transfer from Axial Ligands to  $S_2$ -Excited Tetraphenyl Porphyrins (poster), M. Fujitsuka and \*T. Majima: 11th Sanken International Symposium / 6th nanotechnology center international symposium / 1st MSTEC international symposium, Awaji, Japan, Feb. 4-5, 2008.

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Design of Cyclic Reaction Driven by the Two-color Two-photon Excitation (poster), M. Sakamoto, M. Fujitsuka and \*T. Majima: 11th Sanken International Symposium / 6th nanotechnology center international symposium / 1st MSTEC international symposium, Awaji, Japan, Feb. 4-5, 2008.

Molecular Excitation Chemistry of Supramolecules and Nanomaterials, T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

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Photochemical Formation of Au/Cu Bimetallic Nanoparticles with Different Shapes and Sizes in a PVA Film, \*M. Sakamoto, T. Tachikawa, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

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Single-Molecule Observation of DNA Charge Transfer, \*T. Takada, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Porphyrin Light-Harvesting System Constructed in the Tobacco Mosaic Virus Scaffold, \*M. Endo, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Higher Excited State Chemistry for Light-Energy Conversion (invited), M. Fujitsuka and \*T. Majima: The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science, Daejeon, Korea, Feb. 27-28, 2008.



DNA Devices Based on Charge Transfer in DNA (invited), T. Majima: The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science, Daejeon, Korea, Feb. 27-28, 2008.

#### **Contributions to International Conferences and Journals**

|           |                                                                                                           |
|-----------|-----------------------------------------------------------------------------------------------------------|
| T. Majima | 2007 KOREA-JAPAN Symposium on Frontier Photoscience (Conference Chair)                                    |
| T. Majima | Symposium on “Beam-induced Chemistry of Supramolecules and Nanomaterials 2007 (Conference Chair)          |
| T. Majima | Langmuir Symposium 2007 in Osaka University (Conference Chair)                                            |
| T. Majima | The 9 <sup>th</sup> International Symposium on Eco-materials Processing and Design (Organizing Committee) |

#### **Publications in Domestic Meetings**

|                                                          |           |
|----------------------------------------------------------|-----------|
| Japan Photobiology and Photomedicine Meeting             | 2 papers  |
| Photochemistry Meeting                                   | 11 papers |
| Polymer Meeting                                          | 1 paper   |
| Japan Chemical Society Meeting                           | 10 papers |
| National Meeting of Chemical Society of Japan            | 5 papers  |
| Symposium on Organic Synthesis                           | 1 paper   |
| Symposium on Progress in Organic Reactions and Syntheses | 1 paper   |

#### **Sponsorship**

##### **Grand-in-Aid for Scientific Research (S)**

|           |                                        |             |
|-----------|----------------------------------------|-------------|
| T. Majima | Nanoscience of Photofunctionalized DNA | ¥10,920,000 |
|-----------|----------------------------------------|-------------|

##### **Grand-in-Aid for Basic Scientific Research**

|           |                                                                                                                           |            |
|-----------|---------------------------------------------------------------------------------------------------------------------------|------------|
| T. Majima | Construction of devices for photoelectronic conversion using photochemical control of Tobacco Mosaic Virus supramolecules | ¥1,800,000 |
|-----------|---------------------------------------------------------------------------------------------------------------------------|------------|

##### **Grand-in-Aid for Encouragement of Young Scientists**

|          |                                                   |            |
|----------|---------------------------------------------------|------------|
| K. Kawai | Construction of Nano-DNA Charge-Separation System | ¥1,100,000 |
|----------|---------------------------------------------------|------------|

##### **Entrusted Research**

|           |                        |                                     |            |
|-----------|------------------------|-------------------------------------|------------|
| T. Majima | IDEC Co.<br>Satake Co. | Selection of plastic by laser light | ¥1,690,000 |
|-----------|------------------------|-------------------------------------|------------|

##### **Other Research Fund**

|           |            |                                                                             |            |
|-----------|------------|-----------------------------------------------------------------------------|------------|
| T. Majima | TOYOTA Co. | Hydrogen absorbing alloys with high surface area produced by photoreduction | ¥5,989,000 |
|-----------|------------|-----------------------------------------------------------------------------|------------|

|           |                                    |                                                                         |            |
|-----------|------------------------------------|-------------------------------------------------------------------------|------------|
| T. Majima | Sekisui Chemicals Co.              | Super hydrophilicity by TiO <sub>2</sub> photocatalytic reaction        | ¥999,000   |
| T. Majima | Matsushita Electric Industrial Co. | Study on highly reactive nanostructured TiO <sub>2</sub> photocatalysts | ¥1,732,000 |
| T. Majima | Mitsubishi Chemical Co.            | Basic research on chemical reaction via higher excited states           | ¥2,000,000 |

## Department of Nanobiology

Professor: Katsuyuki TANIZAWA  
Associate Professor: Toshihide OKAJIMA  
Research Associate: Ryousuke NAKASHIMA

### Outlines

Proteins and those complexed with other biomolecules are regarded as nano bio devices. The research of our group is focused on structural and functional studies of the nano bio devices, as well as their applications in the interdisciplinary field. We are also interested in the development of highly sensitive biosensors and construction of nano machines.

### Current Research Project

#### Structural analysis of reaction intermediates formed on catalytic cycle of copper amine oxidase

The catalytic reaction of copper amine oxidase comprises the reductive and oxidative half-reactions, divided on the basis of the redox state of the covalently-bound organic cofactor, topaquinone (TPQ). A substrate amine reduces TPQ to an aminoresorcinol form in the reductive half-reaction. The reduced TPQ is then re-oxidized by molecular oxygen in the following oxidative half-reaction. Previous studies have demonstrated that the TPQ cofactor has certain degree of conformational flexibility within the active site, thereby facilitating facile transfers of  $2\text{H}^+$  and  $2\text{e}^-$  from amine substrate to dioxygen during the catalytic cycle. To freeze trap TPQ in various conformations, we have determined X-ray crystal structures of catalytic intermediates formed in the recombinant enzyme from *Arthrobacter globiformis* and its derivatives site-specifically mutated at a conserved Asn381, whose side chain may interact with the TPQ ring by  $\text{NH}-\pi$  interaction. The structure of wild-type enzyme with TPQ in the substrate-reduced form has revealed that TPQ exists in an “on-copper” conformation, which is probably advantageous for  $1\text{e}^-$ -transfer to  $\text{Cu}^{2+}$  but not for the normal reaction path. The structures of N381A mutant with a 160-fold lower catalytic activity than the wild type show that the TPQ ring is rotated nearly  $180^\circ$  around  $\text{C}_\beta-\text{C}_\gamma$  so that the reactive C5 carbonyl group points opposite to the catalytic base (Asp298) in both the oxidized and substrate-reduced forms. The structures of N381Q mutant with a 10-fold lower catalytic activity than the wild type show that the “wedge-shaped” movement of the TPQ ring, which is important for the proper positioning of the Schiff-base intermediates for abstraction of substrate  $\alpha$ -proton and the following hydrolysis, is prevented in the product Schiff-base intermediate, probably due to the steric hindrance of the side chain of Gln381. Furthermore, stopped-flow measurements of the reductive half-reaction by N381Q mutant have revealed that the step of  $\alpha$ -proton abstraction from the substrate Schiff-base intermediate is significantly retarded in this mutant enzyme. Collectively, these results show that the conformational flexibility of the TPQ ring, regulated at least partly by the side chain of Asn381 through  $\text{NH}-\pi$  interaction, is important for the catalytic reaction to proceed efficiently.

### **Crystallographic analysis of xenobiotic exporters.**

Xenobiotic extruding pumps have recently been known to be widely distributed in living organisms from mammalian to bacteria as a host-defence mechanism in cellular level. These pumps not only confer multidrug resistance of cancer cells and pathogenic bacteria but also cause hereditary diseases through the mutation. We first determined the crystal structure of bacterial major xenobiotic exporter AcrB in 2002 and elucidated the molecular mechanism of xenobiotic export and the structural basis of multidrug recognition by determining the crystal structure of the drug-binding form of AcrB in 2006. In 2007, we continued to solve the substrate-binding form of AcrB with different substrates. In addition, we tried to crystallize the other type of exporters such as TetA.

## **Publications**

### **Original Papers**

Fasciculation and elongation protein zeta-1 (FEZ1) participates in the polarization of hippocampal neuron by controlling the mitochondrial motility., J. Ikuta, A. Maturana, T. Fujita, T. Okajima, K. Tatematsu, K. Tanizawa, and S. Kuroda.: *Biochem. Biophys. Res. Commun.*, 353 (2007) 127-132.

Axonal guidance protein FEZ1 associates with tubulin and kinesin motor protein to transport mitochondria in neurites of NGF-stimulated PC12 cells., T. Fujita, A. D. Maturana, J. Ikuta, J. Hamada, S. Walchli, T. Suzuki, H. Sawa, M. W. Wooten, T. Okajima, K. Tatematsu, K. Tanizawa, and S. Kuroda.: *Biochem. Biophys. Res. Commun.*, 361 (2007) 605-610.

Trapping of a dopaquinone intermediate in the TPQ cofactor biogenesis in a copper-containing amine oxidase from *Arthrobacter globiformis*., R. H. Moore, M. A. Spies, M. B. Culpepper, T. Murakawa, S. Hirota, T. Okajima, K. Tanizawa, and M. Mure.: *J. Am. Chem. Soc.*, 129 (2007) 11524-11534.

Involvement of MAPK signaling molecules and Runx2 in the NELL1-induced osteoblastic differentiation., N. Bokui, T. Otani, K. Igarashi, J. Kaku, M. Oda, T. Nagaoka, M. Seno, K. Tatematsu, T. Okajima, T. Matsuzaki, K. Ting, K. Tanizawa, and S. Kuroda.: *FEBS Lett.*, 582 (2008) 365-371.

Bio-nanocapsule conjugated with liposomes for in vivo pinpoint delivery of various materials., J. H. Jung, T. Matsuzaki, K. Tatematsu, T. Okajima, K. Tanizawa, and S. Kuroda: *J. Control. Release*, 126 (2008) 255-264.

### **Review Papers**

Development of bio-nano carrier and its application to cancer gene therapy, A. Kondo, S. Kuroda, K. Tanizawa, M. Seno, and M. Ueda: *Biotechnology Journal*, 7 (2007) 41-47.

Bio-nanocapsules for in vivo pinpoint drug delivery, J.-H. Jung, T. Kasuya, K. Tanizawa, and S. Kuroda: *Yakugaku Zasshi*, 127 (2007) 797-805.

### **Patents**

“Biotinylated Nanoparticles for Immunological Assays” S. Hiramatsu, G.-M. Jung, S. Hatahira, D. Kanamori, H. Kadoya, S. Kuroda, and K. Tanizawa: JP 2007-3677.

### **International Conferences**

Structural basis for stereospecific proton abstraction of bacterial copper amine oxidase. (poster), \*T. Okajima, T. Murakawa, Y.-C. Chiu, M. Taki, Y. Yamamoto, H. Hayashi, and K. Tanizawa: 2nd International Symposium on Diffraction Structural Biology 2007 (ISDSB2007), Tokyo, Japan, September 10-13, 2007.

A subtilisin-like protease essential for the biogenesis of quinoxinoprotein amine dehydrogenase (poster), \*T. Okajima, K. Ono, A. Nagami, M. Niiyama, and K. Tanizawa.: Gordon Research Conference on Protein Cofactors, Radicals and Quinones, Ventura, California, U.S.A., January 20-25, 2008.

Conformational flexibility of the TPQ cofactor in bacterial copper amine oxidase. (poster), \*T. Okajima, S. Nakanishi, T. Murakawa, H. Hayashi, and K. Tanizawa.: Gordon Research Conference on Protein Cofactors, Radicals and Quinones, Ventura, California, U.S.A., January 20-25, 2008.

Hydrogen tunneling in bacterial copper amine oxidase reaction (poster), \*T. Murakawa, T. Okajima, S. Nakanishi, H. Hayashi, and K. Tanizawa: Gordon Research Conference on Protein Cofactors, Radicals and Quinones, Ventura, California, U.S.A., January 20-25, 2008.

Response regulator YycF essential for bacterial growth: X-ray crystal structure of the DNA-binding domain and its PhoB-like DNA recognition. (poster), \*A. Tada, T. Okajima, A. Doi, A. Okada, Y. Gotoh, R. Utsumi, and K. Tanizawa.: 11th Sanken International Symposium/6th Nanotechnology Center International Symposium/1st MSTEC International Symposium, Awaji Yumebutai International Conference Center, Hyogo, Japan, February 4-5, 2008.

### **Publications in Domestic Meetings**

Joint Annual Meeting of the Molecular Biology Society of Japan and the Japanese Biochemical Society (BMB2007) 18 papers

Annual Meeting of the Crystallographic Society of Japan 1 paper

Annual Meeting of Japan Society for Bioscience, Biotechnology, and Agrochemistry 1 paper

11th Spring-8 Symposium 1 paper

## Sponsorships

### Grant-in-Aid for Scientific Research (B)

|             |                                                                                               |            |
|-------------|-----------------------------------------------------------------------------------------------|------------|
| K. Tanizawa | Mechanisms of Biosynthesis and Catalysis of Built-in Type Quinone Cofactor                    | ¥3,380,000 |
| T. Okajima  | Mechanism of Proton and Electron Transfer in Enzyme Containing Built-in Type Quinone Cofactor | ¥3,900,000 |

### Grant-in-Aid for Young Scientists (B)

|              |                                                |            |
|--------------|------------------------------------------------|------------|
| R. Nakashima | Crystallization of tetracycline efflux protein | ¥1,560,000 |
|--------------|------------------------------------------------|------------|

### Entrusted Research

|             |                                                                  |                                                                                                                                                                                                                                 |             |
|-------------|------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| K. Tanizawa | Japan Science and Technology Agency (CREST)                      | Creation of Functional Materials/ System that Utilize Nano Biotechnology for Realizing a Noninvasive Medical Treatment System: Novel Cell-selective Gene Delivery System Using Intracellular Signal-responsive Molecular System | ¥7,540,000  |
| K. Tanizawa | Bio-oriented Technology Research Advancement Institution (BRAIN) | Development of Innovative and Hypersensitive Bio-sensing Technology Using Yeast-derived Bio-nanocapsule                                                                                                                         | ¥20,000,000 |
| T. Okajima  | Bio-oriented Technology Research Advancement Institution (BRAIN) | Development of Drugs Inhibiting Bacterial Signal Transduction Based on X-ray Crystal Structures                                                                                                                                 | ¥7,000,000  |

### Other Research Fund

|             |                     |                                |          |
|-------------|---------------------|--------------------------------|----------|
| K. Tanizawa | Vitamin B Committee | Research on Built-in Cofactors | ¥250,000 |
|-------------|---------------------|--------------------------------|----------|

## Department of Nanosystem Design

Guest Professor: Ryusuke NISHITANI (2007. 4.1-2007.6.30)

### Outlines

The local optical and electronic analysis of materials on a nanometer scale is indispensable for the development of nanometer electronics. In this study, we have developed a system of STM-induced luminescence measurement, and carried out spectroscopic measurements of molecular luminescence of organic films for various combinations of the tips and the substrates.

### Achievement

We investigate scanning tunneling microscope (STM)-excited fluorescence from porphyrin thin films on various combinations of substrates (Pt, Ag, Au and ITO) and PtIr, Ag and Au tips. The measured intensities of porphyrin-fluorescence  $I$  for the substrates are  $I(\text{ITO}) < I(\text{Pt}) < I(\text{Ag})$ . These molecular-fluorescence intensities are found to be comparable to plasmon-mediated light emission from the corresponding pristine substrates. We calculate relative electromagnetic-field powers in the tip-substrate gaps, which are in consistent with the observed of the plasmon-mediated light emissions. The material dependences and calculated gap size dependences elucidate that, (1) enhancement of the light emissions for the PtIr-tip/Pt cavity is stronger than the Ag tip/ITO one indicating that the effect of the field confinement for the former is stronger than that of the intense plasmon field of the Ag tip and (2) in nanoscale metal cavities where one of the electrode is Ag or Au, highly intense electromagnetic field is established by plasmonic gap modes and thus intense plasmon-mediated light and molecular fluorescence can be emitted. This supports/extends our previous proposal of Surface plasmons-Enhanced Molecular Fluorescence (SEMF). We also find rather strong energy forbidden fluorescence of porphyrin for an Au-tip/porphyrin/Au cavity which we attribute to two photons excitation under the extremely strong field in the nanoscale plasmonic cavity.

### Publication

#### Original Papers

Bias Dependence of Tunneling-Electron-Induced Molecular Fluorescence from Porphyrin Films on Noble-Metal Substrates, H. Liu, Y. Ie, R. Nishitani, Y. Aso and H. Iwasaki, Phys. Rev. B, 75 (2007) pp. 115429-1 -115429-5.

STM Tip-Enhanced Photoluminescence from Porphyrin Film, R. Nishitani, H. Liu, A. Kasuya, H. Miyahira, T. Kawahara and H. IWASAKI, Surf. Sci., 601 (2007) pp. 3601-3604.

Study on Enhancement of Tunneling-Induced Fluorescence from Porphyrin Film by Substrate Plasmon, R. Nishitani, H. Liu, A. Kasuya, H. Iwasaki, J. Phys., 61 (2007) pp. 879.

## **International Conference**

Cavity Effect on Molecular Fluorescence of a Porphyrin Film Induced by Tunneling electrons, H. Liu, Y. Ie, Y. Aso, K. Sudoh, H. Iwasaki, R. Nishitani, ChinaNano2007, Beijing 2007.6.4-7.

Cavity effect in STM junction on the tunneling-induced molecular fluorescence , R. Nishitani, H. Liu, H. Iwasaki, Korea-Japan Joint Forum (KJF) 2007 on Organic Materials for Electronics and Photonics, Seoul, Korea, Sep 27-29, 2007.

Cavity effect in STM junction on the tunneling-induced molecular fluorescence, R. Nishitani, H. Liu, H. Iwasaki, 9th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-9), Tokyo, Japan, Nov 11-15, 2007.



## Department of Nanosystem Design

Guest Associate professor: Mitsumasa Taguchi (2007.7.1-2007.9.30)

### Outlines

Halogenated organic chemicals such as polychlorodibenzo-*p*-dioxin, polychlorobiphenyls and hexachlorobenzene are toxic pollutants characterized by persistence and accumulation to the body of aquatic animals. These pollutants are not readily treated by advanced oxidation treatments such as ozone/UV, ozone/hydrogen peroxide and so on. The ionizing radiation, however, is expected as a good technique for treating halogenated organic compounds because it can homogeneously and quantitatively produce reactive species that can oxidize target substances. Room temperature ionic liquids (RTILs) have unique properties such as nonvolatile, nonflammable, high polarity, and wide electrochemical window<sup>1)</sup>. We paid attention to the combination method of ionizing radiation and RTILs as a new environmental conservation technology for the treatment of halogenated chemicals.

### Achievement

In our research, the behavior and reactivity of solvated electrons were studied in the Coulomb field of RTILs which are composed of cations and anions. The six kind ionic liquids of DEMMA-TFSI, DEMMA-BF<sub>4</sub>, TPA-TFSI, BMI-TFSI, MPPr-TFSI and DEMA-TSAC were used in the experiment. Chlorophenols (CP) were used as a probe of the solvated electrons because react with the electron to form phenol, of which the *G*-value and the rate constant in *tert*-butanol aqueous solution have been estimated to be 0.7 and  $4.4 \times 10^8 \text{ mol}^{-1} \text{ s dm}^3$ , respectively (Getoff et al., 1988; Schmid et al., 1997.). In this study, the reactivity of the solvated electrons in RTILs is investigated by the long-time scale radiolysis with gamma-ray and the short-time scale radiolysis with electron pulse. It is found that *G*(-CP) and *G*(Phenol) in aromatic RTILs were lower than that in aliphatic one. The ratios of *G*(Phenol) / *G*(-CP) were not affected by the substituted position of chlorine group on CP in RTILs. The transient species in RTILs were observed for optical absorption with a peak at 1100 nm by the pulse radiolysis method, and are assumed to be the solvated electrons. CP was efficiently reduced by the solvated electrons in DEMMA-TFSI, which have the physical properties adequate to the waste water treatment process.

## **Department of Department of Nanosystem Design**

Guest Professor: Masanori KOHYAMA (2007.10.1-2007.12.31)

### **Outlines**

We have made detailed discussion on the possible collaboration between experiments and ab initio calculations on the interactions between metallic nano-clusters and organic molecules. We have pointed out the following important issues; intrinsic interactions between metal surfaces and molecules, effects of nano-clusters, effects of kinds and properties of molecules and resultant bulk properties of nano-composites of metallic particles and molecules. We have made discussion on the experiments and ab initio calculations to clarify each issue.

### **Achievement**

About the intrinsic interactions between metallic surfaces and molecules, there are von der Waals interactions, image interactions induced by polar molecules, and strong orbital hybridization coupled with charge transfer. We have considered how these interactions dominate the bulk properties of nano-composites of metallic nano-clusters and molecules as well as the effects of nano-clusters and kinds of molecules. Finally, we have considered a plan of experimental and theoretical detection on the above issues.

## **Department of Nanosystem Design**

Guest Professor:                      Tadatomi NISHIKUBO (2008.1.1-2008.3.31)

### **Outlines**

An extreme ultraviolet (EUV) exposure is promising light source for semiconductor devices after the 22 nm node. However, it is very difficult to overcome the shrinkage of line edge roughness. Low molecular weight resists have attracted attentions as a one of the solution. Therefore newly synthesized polyacenic polyphenol compounds “Noria” was studied.

### **Achievement**

Noria resist was characterized by means of 75 keV electron beam exposure system. As a result, the pattern formation less than 70 nm was succeeded in through optimizations of additives and baking condition. In addition, etching rates were also evaluated, and it became clear to have similar etching rate to polyhydroxy styrene resists.

# Division of Beam Science for Nanotechnology

## Outlines

The division of beam science for nanotechnology is composed of five research departments: beam science for nanofabrication, quantum beams for nanotechnology, beam processing for nanotechnology, advanced nanofabrication, and ultra-fast spectroscopy of nanostructures. Quantum beam science is one of the most important fields for nanoscience and nanotechnology. The researches are performing by using ultra-short electron beam, slow positron beam, ion beam, electron lithography and so on. The studies such as time-space reaction analysis with ultra-short electron beam, nano-structure analysis with slow positron beam and nano-beam process, are expected for ultimate nanofabrication and a new nano-beam science.

## Achievements

- Development of laser photocathode RF linear accelerator
- Generation of femtosecond electron source
- Femtosecond pulse radiolysis based on equivalent velocity spectroscopy
- Double-decker electron accelerator and attosecond pulse radiolysis
- Primary Process of Quantum Beam-Induced Nanofabrication
- Analysis of spur reactions for nanofabrication
- Radiation chemistry of ionic liquids
- Improvement of L-band linear accelerator for nanoscience
- Generation of intense slow-positron beam
- Study of annihilation process of positrons in polymeric materials using AMOC
- Study of primary radiation reactions in resists using positron annihilation technique
- Single-particle induced chemical reactions and nanotechnology
- Study of physical properties of single molecular by using quantum beam
- Study of nano-process with quantum beam
- Modeling of nano-process in resist

## Department of Beam Science for Nanofabrication

Professor: Yoichi YOSHIDA  
Associate Professor: Jinfeng YANG  
Assistant Professor: Takafumi KONDOH  
Graduate Students: Kouichi KAN, Masayoshi HIROSE, Akira ASANO,  
Haruki TANAKA, Hiroaki KASHIMA  
Research Students: Shiya IZAWA, Yoshihiko NOMURA  
Support Staff: Mie TERASHITA

### Outline

A femtosecond/attosecond pulse radiolysis based on a photocathode electron beam accelerator is being developed for the study of such ultrafast reactions in nano-space. The study of ultrafast reactions in nano-space of the materials is very important for the development of ultimate fabrication process with quantum beam for the next nanotechnology (e.g. EUV lithography).

In 2007, the equivalent velocity spectroscopy (EVS) based pulse radiolysis system was constructed to avoid the degradation of time resolution due to the velocity difference between the analyzing light and the electron in sample. In EVS, the electron bunch is rotated into an angle as same as the injection angle between the electron beam and the analyzing light. The technique of rotating the electron bunch was developed by rotating the longitudinal phase-space of the electron bunch before it passes through the bunch compressor. The rotation angle of the electron bunch was successfully measured with a streak camera technique. Furthermore, a picosecond pulse radiolysis system based on the photocathode electron beam accelerator was constructed for the study of the dynamics of solvated electrons in ionic liquids and geminate ion recombination in liquid alkanes. The attosecond electron bunch generation and the coherent ionization were studied theoretically.

### Current Research Programs

#### 1. Equivalent velocity spectroscopy based pulse radiolysis – Electron bunch rotation -

In EVS, the electron beam and the analyzing laser light are injected into the sample with an angle ( $\theta$ ) which is determined by the refractive index of the sample, to avoid the degradation of time resolution due to the velocity difference between the analyzing light and the electron in sample. However, the electron bunch should be rotated with a same angle to make an overlap of the electron bunch with the laser pulse in sample. In order to rotate the electron bunch, a magnetic bunch compressor, which was constructed with two 45°-bending magnets and four quadrupole magnets (two pairs) to provide a necessary path length dependence on energy, was used. The electron beam generated from the rf gun is accelerated by the linear accelerator up to 32 MeV with energy-phase correlation in the bunch by re-phasing the RF phase of the linac before it is transported into the bunch compressor. The necessary rotation angle of the electron bunch is achieved by passing the electron beam through the compressor and optimizing the magnetic fields of the quadrupole magnets. The rotation angle of the bunch was successfully measured by mean of a streak camera technique.

As the results, the electron bunch was able to be rotated from 0 to 67 degree by

changing the linac phase. The time resolution of the pulse radiolysis was improved during the rotation of the electron bunch. It indicated that the EVS is a powerful tool to improve the time resolution of pulse radiolysis.

## 2. Pulse radiolysis study of ionic liquids

In the last few years, ionic liquids (ILs), as new solvents, were rapidly finding new applications in chemical synthesis, electrochemistry, separation chemistry and other areas. The chemical reactivity in ionic liquids has been begun to be studied. Nanosecond pulse radiolysis studies of ionic liquids have been published. The researches indicate that, for the imidazolium ionic liquids, the electrons produced by ionization are rapidly scavenged by the solvent molecules before they become fully solvated, while the electrons in the ammonium ionic liquids are solvated quickly to form the solvated electrons. The electrons solvated in ammonium ionic liquids have a very broad absorption band peaking over 1000 nm with a molar absorption coefficient of  $1.9\text{--}2.3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  and a radiolytic yield ( $G$ ) of  $0.7\text{--}0.8 \times 10^{-7} \text{ mol J}^{-1}$  in the nanosecond time region. The solvated electrons in ionic liquids decay with a rate constant of  $10^6\text{--}10^7 \text{ s}^{-1}$  which is dependent on the kind of ionic liquids. The reactions of the solvated electron with some aromatic scavengers such as benzophenone and pyrene are diffusion-limited, with rate constants of the order of magnitude of  $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . On the other hand, the dry electron capture by scavengers was found to be very fast in ionic liquids. Therefore, the study at picosecond range of the primary reactions and the chemical kinetics in ionic liquids (e.g. formation process of solvated electron, reaction and kinetics of dry electron) is essential in order to design the ionic liquids for new applications.

A picosecond pulse radiolysis based on a laser-driven photocathode electron accelerator and an all solid-state Nd:YLF picosecond laser has been constructed in Osaka University for studying ultrafast chemical kinetics and primary processes of radiation chemistry. The time resolution of the pulse radiolysis was 15 ps by using a 2-ps-long-bunch electron beam with energy of 32 MeV, a 2.3-ps time-synchronized laser light and a 10-mm-thick sample. It was successfully used to study the dynamics of the solvated electrons in ionic liquids. First observation of picosecond dynamics in irradiated ionic liquid DEMMA-TFSI, i.e. solvation and reaction of electrons produced by ionization in ionic liquid, was reported. It was found that the electron produced by ionization is fully solvated in ionic liquid with a rate constant of  $3.9 \times 10^{10} \text{ s}^{-1}$  (26 ps). The radiolytic yield ( $G$ ) of the solvated electrons in the picosecond time region is  $1.2 \times 10^{-7} \text{ mol J}^{-1}$ . The dry electron reacts with aromatic electron scavenger, such as pyrene and biphenyl. The  $C_{37}$  value in DEMMA-TFSI in the picosecond time region was obtained to be  $0.054 \text{ mol dm}^{-3}$  for pyrene and  $0.108 \text{ mol dm}^{-3}$  for biphenyl. The rate constant of the reaction of the dry electron with scavenger was estimated to be  $7.9 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for pyrene and  $3.8 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for biphenyl, which are about one order of magnitude higher than that of the solvation dynamics, and three orders of magnitude higher than that of the solvated electron reactions. The high rate constants of dry electron reactions show that the ionic liquid is a new kind of solvent.

## 3. Geminate ion recombination in liquid alkanes

The geminate ion recombination, as a most important primary process in radiation chemistry, has been studied for a long time by many researchers. In regard to the kinetics of the geminate ion recombination, the geminate decay and the formation of

excited states from the geminate ion recombination have been measured by using nanosecond and picosecond pulse radiolysis, and analyzed theoretically with the Smoluchowski equation based on the diffusion theory. However, most pulse radiolysis studies of the geminate ion recombination in n-dodecane were done by measuring the transient absorption kinetics of cation radicals at near 800 nm or electrons at >1000 nm.

In our research, the geminate ion recombination was studied by using the picosecond pulse radiolysis at the wavelength of 523 nm. At this wavelength, not only the kinetics of the cation radical are observed, but also the formation of excited states due to the geminate ion recombination and the decay of the excited states can be studied, because of the overlap of the cation radical and the excited state absorbance. In our experiments, the kinetics of the cation radical in n-dodecane and n-hexane were observed and compared with the theoretical simulation based on the Smoluchowski equation. It is found that the experimental data are in good agreement with the theoretical description at > 50 ps. The ratio of the yields of the excited states formed by the direct excitation/energy transfer was estimated to be 10% in n-dodecane, and 17% in n-hexane.

## **Publications**

### **Original Papers**

Bunch Length Measurement using Spectral Width of Monochromatic Synchrotron Radiation, A. Ogata, T. Kondoh, J. Yang, A. Yoshida, Y. Yoshida: Nucl. Instrum. Method A, 578 (2007) 348-350.

LWFA of Atto-Second Bunches for Pulse Radiolysis, A. Ogata, T. Kondoh, J. Yang, A. Yoshida, Y. Yoshida: Int. J. Modern. Phys., 21 (3) (2007) 447-458.

Subpicosecond pulse radiolysis in liquid methyl-substituted benzene derivatives, K. Okamoto, T. Kozawa, A. Saeki, Y. Yoshida, S. Tagawa: Radiat. Phys. Chem., 76 (2007) 818-826.

Electron photodetachment from iodide in ionic liquids through charge-transfer-to-solvated band excitation, R. Katoh, Y. Yoshida, Y. Katsumura, K. Takahashi: J. Phys. Chem. B, 111 (2007) 4770-4774.

### **International Conferences**

Femtosecond Electron Beam Dynamics in Photocathode Accelerator (poster), J. Yang, K. Kan, T. Kondoh, Y. Yoshida, S. Tagawa: Particle Accelerator Conference 2007.

Dynamic Optical Modulation of the Electron Beam for the High Performance Intensity Modulated Radiation Therapy (poster), T. Kondoh, H. Kashima, J. Yang, Y. Yoshida: Particle Accelerator Conference 2007.

Simulation Study on Attosecond Electron Bunch Generation (poster), K. Kan, T. Kondoh, J. Yang, Y. Yoshida: Particle Accelerator Conference 2007.

Attosecond and Femtosecond Pulse Radiolysis by using Laser Photocathode rf Gun

Linac (invited), Y. Yoshida, J. Yang, T. Kondoh: 7th International Symposium on Advanced Science Research – Charged Particle and Photon Interactions with Matter.

Picosecond and Femtosecond Pulse Radiolysis Study on Solvated Electrons in Ionic Liquids (poster), J. Yang, T. Kondoh, R. Nagaishi, Y. Yoshida: 7th International Symposium on Advanced Science Research – Charged Particle and Photon Interactions with Matter.

Reactions of Solvated Electrons in Ionic Liquid Diethylmethyl (2-methoxy) ammonium - Bis (trifluoromethanesulfonyl) imide (poster), A. Asano, T. Kondoh, J. Yang, R. Nagaishi, K. Takahashi, Y. Yoshida: 7th International Symposium on Advanced Science Research – Charged Particle and Photon Interactions with Matter.

Dynamic Optical Modulation of Electron Beam on a Photocathode RF Gun toward the Intensity Modulated Radiation Therapy (IMRT) (poster), T. Kondoh, H. Kashima, J. Yang, Y. Yoshida, S. Tagawa: 7th International Symposium on Advanced Science Research – Charged Particle and Photon Interactions with Matter.

Looking for Dielectron: Reactions of Electrons in Ionic Liquid (poster), K. Takahashi, Y. Hiejima, R. Katoh, Y. Yoshida, Y. Katsumura: 7th International Symposium on Advanced Science Research – Charged Particle and Photon Interactions with Matter.

Decomposition of Halogenated Organic Chemicals in Room Temperature Ionic Liquids by Ionizing Radiation (poster), A. Kimura, M. Taguchi, T. Kondoh, J. Yang, Y. Yoshida, K. Hirota: 7th International Symposium on Advanced Science Research – Charged Particle and Photon Interactions with Matter.

Photocathode based Femtosecond Electron Source (poster), J. Yang, K. Kan, T. Kondoh, K. Norizawa, Y. Yoshida, K. Tanimura: 11<sup>th</sup> SANKEN International Symposium 2007 / SANKEN Nanotechnology Symposium / SANKEN MSTEC Symposium.

The Study of Optical Modulation of Electron Beam on a Photocathode RF Gun for Intensity Modulated Radiation Therapy (IMRT) (poster), T. Kondoh, H. Kashima, J. Yang, K. Kan, Y. Yoshida, S. Tagawa: 11<sup>th</sup> SANKEN International Symposium 2007 / SANKEN Nanotechnology Symposium / SANKEN MSTEC Symposium.

Collective Phenomena Induced by Attosecond Electron Bunches (poster), A. Ogata, T. Kondoh, J. Yang, Y. Yoshida: 11<sup>th</sup> SANKEN International Symposium 2007 / SANKEN Nanotechnology Symposium / SANKEN MSTEC Symposium.

Pulse Radiolysis Study of MgSO<sub>4</sub> · 7H<sub>2</sub>O Single Crystal (poster), K. Norizawa, T. Kondoh, J. Yang, Y. Yoshida: 11<sup>th</sup> SANKEN International Symposium 2007 / SANKEN Nanotechnology Symposium / SANKEN MSTEC Symposium.

#### **Publications in Domestic Meetings**

Symposium on Advanced Accelerator  
The Japan Society of Radiation Chemistry  
The Particle Accelerator Society of Japan

1 paper  
6 papers  
5 papers



|                                |          |
|--------------------------------|----------|
| Atomic Energy Society of Japan | 4 papers |
| Symposium on RF Electron Gun   | 4 papers |
| Symposium on TIARA             | 1 paper  |

## Academic Degrees

### Master Degree of Engineering

Akira Asano      Study on radiation chemistry in ionic liquids

## Sponsorship

### Grant-in-Aid for Basic Research (A)

|            |                                                                                                 |             |
|------------|-------------------------------------------------------------------------------------------------|-------------|
| Y. Yoshida | Research on Equivalent Velocity Spectroscope for Subfemtosecond and Attosecond Pulse Radiolysis | ¥13,130,000 |
|------------|-------------------------------------------------------------------------------------------------|-------------|

### Grant-in-Aid for Basic Research (C)

|         |                                              |            |
|---------|----------------------------------------------|------------|
| J. Yang | High LET based on Heavy Ion Pulse Radiolysis | ¥2,340,000 |
|---------|----------------------------------------------|------------|

## Collaborative Researches

|            |                                            |                                                                           |            |
|------------|--------------------------------------------|---------------------------------------------------------------------------|------------|
| J. Yang    | KEK                                        | Development of photocathode femtosecond electron source                   | ¥1,800,000 |
| Y. Yoshida | JAERI Tokai                                | High time resolution study on radiation-induced reaction in nanostructure |            |
|            | JAERI Tokai                                | Pulse radiolysis study of Ionic Liquid                                    |            |
|            | JAERI Takasaki                             | Mechanism of micro sphere generation in phenol solution                   |            |
|            | JAERI Takasaki                             | Radical study by using ion pulse radiolysis                               |            |
|            | National Institute of Radiological Science | Beam control technique on the intensity modified radiation therapy        |            |

## Department of Quantum Beams for Nanotechnology

Professor: Goro ISOYAMA  
Associate Professor: Yoshihide HONDA  
Research Associate: Norio KIMURA

### Outline

In this department, we conduct research on development of new measurement methods in the nanometer range using quantum beams, which are expected to form bases for nanotechnology, and on their applications as well as on development of quantum beams. To put it concretely, we are developing a highly intense and bright positron beam using an electron linac and its applications to materials science. Positrons have a nature to concentrate in holes and free volumes in materials and consequently measurements using positrons are widely received as an effective method to analyze sizes and distributions of free volumes. The positron beam is highly expected to play an important role in analyzing not only the sizes but also the distributions of nanometer size spaces and free volumes in porous materials such as polymers. We conduct research for better understanding interactions of positrons and positroniums, which are formed by an electron and a positron as a bound state, with materials, and for analyzing free volumes, surfaces and interfaces in thin polymer films, and finally for developing new materials. Since high-quality positron beams are necessary for conducting such researches, we also make studies on production of intense, bright, and short-pulsed slow positron beams using an electron linac, and on development of new measurement methods. We also take part in management and operation of the Radiation Laboratory, which has the experimental apparatuses for these studies.

### Current Research Projects

#### 1. Commissioning of the S-band Linac

The S-band linac, which has been used for production of a slow positron beam, has three acceleration tubes and the nominal energy of the accelerated electron beam is 150 MeV. So far the stability of the electric power fed to the linac has not been enough because of the electric noise. Rearrangement of the circuit, especially for ground lines, has been carried out, however, such procedures were not effective. In the previous year, a frame in which the power supply, modulator and pulse forming network are equipped, and DC power source were renewed. The actual equipment of the parts into the frame was carried out in this year. A frame of the discharge circuit of Klystron was also renewed because of the leakage of oil.

#### 2. Development of New AMOC System Based on Angular Correlation

In the measurements for polymer electrolyte membrane (PEM), Nafion-117, S-parameter, which is an index representing Doppler broadening of photopeak, has found to be a sensitive parameter to express the degradation of the membrane rather than lifetime of o-Ps. However, the S-parameter would be affected by both annihilation  $\gamma$ -rays originating free positron and o-Ps. To identify which effect is dominant in S-parameter, AMOC (age-momentum correlation) measurement was

carried out. In the usual measurement for AMOC, high purity Germanium detector (HPGe) is usually used, however, the resolution of HPGe is not so good as angular correlation. Because of this reason, we designed a new measuring system based on AMOC with angular correlation. In such a system, intense positron source such as linac based slow positron beam, is required to get proper counting rate. The new system is aiming at both high momentum resolution of annihilated electron and high time resolution. Designing the new system, the problem to be resolved is the size of scintillator, BaF<sub>2</sub> in the present case. The thickness of the BaF<sub>2</sub> depends on the angular resolution. The resolution of the system basically depends on the many elements such as spread and inclination of the trajectory of secondary electrons in the BaF<sub>2</sub>, ADC resolution, amplification factor, etc.. In this work, we numerically investigated the ability of the new system by comparing the resolution of energy spectrum with the spread of the truck mentioned above. The results showed that if the thickness of the scintillator was taken to be 1 cm and positioned 1 m apart from the source, the better resolution would be obtained.

### **3. Investigation of Degradation Process of Polymer Electrolyte Membrane by Using Positron**

Understanding deterioration mechanism of polymer electrolyte membrane (PEM) for fuel cell is very important from the view of future development of robust membranes with longer lifetime in actual fuel cell environment. Especially, the chemical and the structural changes of PEM have already been investigated by using conventional techniques such as X-ray diffraction, infrared spectroscopy, electron spin resonance (ESR) techniques, etc.. A positron which is sensitive to such changes can be used to analyze deteriorating process in PEM. The changes in the structure or the electronic state of the polymer may be reflected as change in the lifetime and relative intensity of *o*-Ps or line-shape parameter (S-parameter) of the photopeak of annihilation  $\gamma$ -ray. We have already investigated thermally degraded Nafion-117 by using positron annihilation spectroscopy (PAS) together with proton conductivity measurement. The degradation of PEM is usually taken as the deterioration of the proton conductivity; we in this work too have considered the same. In the current work to investigate the influence of radicals on proton conductivity, the relationship between proton conductivity and PAS related parameters was measured. In the chemical degradation of PEM studied by using Fenton reagent, it has been thought that the main site for degradation is the scission of the backbone of PEM caused by chemical reactions of radicals produced in Fenton reaction. However, this method introduces iron ions into PEM and affects the chemical property of PEM as well as proton conductivity. To avoid effect due to the presence of iron, in this work, we adopted  $\gamma$ -ray irradiation to degrade the PEM, and investigated the relationship between proton conductivity and positron annihilation related parameters such as lifetimes of positron and line-shape parameter. The results showed that there was a small change in lifetime of positron/positronium, whereas the S-parameter showed fairly good correlation with proton conductivity. Also no significant change was observed in ESR spectrum, whereas S-parameter showed big change in lower absorbed dose region. This change would be attributed to the change of chemical state close to the sulfonic site, affecting the conductivity as well as

S-parameter. Further studies to investigate the chemical reaction causing this change are underway.

#### **4. Influence of Functional Groups on Positronium Formation in Polymers**

The reductive cleavage of the carbon-halogen bond in alkyl halides upon addition of one electron is a simplest example of dissociative electron-transfer reactions. An important mechanistic and practical issue is whether the reaction is concerted or stepwise. Recent theoretical studies show that electron attachment and bond dissociation are completed within a few hundred femto-seconds (fs). The application of fs technique to study the dissociative electron attachment reaction has, to my knowledge, not been attempted so far. Recently positron annihilation spectroscopy has been used to estimate the size of nanoscale open pore, which is often called free volume hole, in polymers. Injection of positron as well as electron induces ionization. Positronium takes place between thermalized positron and electron. This reaction is competitive with recombination of ion and electron, scavenging of electron by halogenated alkyl. Hence, by taking into account of positronium formation taking place within several picoseconds after positron injection, these competitive reactions would be investigated by analyzing positronium formation. This feasibility study is carried out in this study.

### **Publications**

#### **Original Papers**

Study of annihilation processes of positrons in polystyrene-related polymers, Y. Honda, T. Shimada, M. Tashiro, N. Kimura, Y. Yoshida, G. Isoyama and S. Tagawa, *Radiat. Phys. Chem.* **76**(2007) 169-171.

Analysis of Swelling Process of Protein by Positron Annihilation Lifetime Spectroscopy and Differential Scanning Calorimetry, Y. Akiyama, Y. Shibahara, S. Takeda, Y. Izumi, Y. Honda, S. Tagawa, S. Nishijima, *J. Polym. Sci. Part B: Polym. Phys.* **45**(2007)2031-2037.

Analysis of thermal degradation process of Nafion-117 with age-momentum correlation method, Y. Shibahara, Y. Akiyama, H. Miyauchi, Y. Izumi, S. Nishijima, Y. Honda, N. Kimura, S. Tagawa, G. Isoyama, *J. Polym. Sci. Part B: Polym. Phys.* **46**(2008)1-7.

Direct evidence of positronium trapping in the cavity of crown ether, Y. Shibahara, Y. Honda, Y. Akiyama, Y. Izumi, S. Tagawa, S. Nishijima, *Chem. Phys. Lett.* **450**(2008)350-354.

#### **International Conferences**

Study on Polymer Electrolyte Membrane for Fuel Cell by Using AMOC Technique, Y. Honda, Y. Shibahara, Y. Akiyama, N. Kimura, G. Isoyama, S. Tagawa, S. Takeda, Y. Izumi, S. Nishijima, *Phys. Stat. Solidi (C)* **4**(2007)3735-3738.

The investigation of Swollen Process in Gelatin Gel by Using Positron Annihilation Spectroscopy, Y. Akiyama, Y. Shibahara, S. Takeda, Y. Izumi, Y. Honda, S. Nishijima, *Phys. Stat. Solidi (C)* **4**(2007)3920-3923.

Structural analysis of macrocyclic polyether with positron annihilation measurement, Y. Shibahara, Y. Akiyama, Y. Izumi, Y. Honda, S. Tagawa, S. Nishijima, The 17<sup>th</sup> Iketani Conference: The Doyama Symposium (Tokyo, 2007).

Study on hydrocarbon based electrolyte membrane by using positron annihilation technique, H. Miyauchi, Y. Shibahara, Y. Akiyama, Y. Izumi, S. Nishijima, Y. Honda, N. Kimura, G. Isoyama, S. Tagawa, The 17<sup>th</sup> Iketani Conference: The Doyama Symposium (Tokyo, 2007)

Analysis of Radiation Induced Degradation in a Polymer Electrolyte Membrane with Positron, Y. Honda, N. Kimura, P. K. Pujari, G. Isoyama, S. Tagawa, H. Miyauchi, Y. Shibahara, Y. Akiyama, Y. Izumi, S. Nishijima, 11<sup>th</sup> SANKEN International Symposium/ 6<sup>th</sup> Nanotechnology Center International Symposium/ 1<sup>st</sup> MSTEC International Symposium, Awaji, Feb. 4-5, 2008.

Study on Polymer Electrolyte Membrane with Positron Annihilation Spectroscopy, Y. Honda, N. Kimura, G. Isoyama, S. Tagawa, H. Miyauchi, Y. Shibahara, Y. Akiyama, Y. Izumi, S. Nishijima, 3<sup>rd</sup> CNU-SANKEN Joint Symposium on Advanced Materials Science, Daejeon, Korea, Feb. 27-28, 2008.

#### **Publications in Domestic Meetings**

|                                           |          |
|-------------------------------------------|----------|
| Meeting of Electrochemical Society        | 2 papers |
| Meeting of Atomic Energy Society of Japan | 2 papers |

#### **Grant-in-Aid for Scientific Research (\*) (\*)**

|          |                                                          |            |
|----------|----------------------------------------------------------|------------|
| Y. Honda | Evaluation of polymer electrolyte membrane with positron | ¥3,640,000 |
|----------|----------------------------------------------------------|------------|

## Department of Beam Science for Nanotechnology

|                      |                  |
|----------------------|------------------|
| Professor:           | Seiichi TAGAWA   |
| Associate Professor: | Takahiro KOZAWA  |
| Specially Appointed  | Kazumasa OKAMOTO |
| Assistant Professor: |                  |

### Outline

The targets of the present department are the establishment of initiatives of quantum beams for nanoscience and nanotechnology. Quantum beams mean both beams such as photons and beams inducing interactions with materials in the nanoscopic level of quantum mechanics. The beams potentially have applicability for imaging with ultra fine patterns, and the present department aims to use the fine patterns as the probes for nano-structured material sciences and devices.

### Current Research Projects

#### **Reaction Mechanisms in Polymeric Materials for Micro- and Nano-electronics**

Chemically amplified resist system is one of the most practical candidates in the future technology in semiconductor fabrication. Reaction mechanisms in the system are analyzed upon exposure to electron beams, X-rays, and laser beams to design a new lithography technique in the present program.

#### **Radiation-Induced Reactions in Nanoscopic Region**

Electron beam lithography has the highest resolution among top-down writing systems. The ultimate spatial resolution is closely related to the reaction mechanism of resist materials. The relation between a spatial resolution and reaction mechanisms was investigated by a subpicosecond pulse radiolysis.

#### **Nanosize distributions of Polymer Matrices and Acid Generators in Resist Films**

The feature sizes in micro-fabrication have shrunk with the progresses in lithography technology. The decrease in deviation of resist pattern has been also needed to molecular size. Thus, distribution of photo-acid generator (PAG) and orientation of polymer matrix have been important issues. X-ray reflectivity measurements were carried out to understand PAG distribution and polymer orientation from the resist film density map in-depth.

### Publications

#### **Original Papers**

Dissolution characteristics and reaction kinetics of molecular resists for extreme-ultraviolet lithography, M. Toriumi, J. J. Santillan, T. Itani, T. Kozawa, S. Tagawa: J. Vac. Sci. Technol. B, 25 (6) (2007) 2486-2489.

Image contrast slope and line edge roughness of chemically amplified resists for

postoptical lithography, T. Kozawa, S. Tagawa, J. J. Santillan, M. Toriumi, T. Itani: J. Vac. Sci. Technol. B, 25 (6) (2007) 2295-2300.

Stroboscopic Picosecond Pulse Radiolysis Using Near-Ultraviolet-Enhanced Femtosecond Continuum Generated by CaF<sub>2</sub>, A. Saeki, T. Kozawa, K. Okamoto, S. Tagawa: Jpn. J. Appl. Phys., 46 (1) (2007) 407-411.

Dependence of Absorption Coefficient and Acid Generation Efficiency on Acid Generator Concentration in Chemically Amplified Resist for Extreme Ultraviolet Resists, R. Hirose, T. Kozawa, S. Tagawa, T. Kai, T. Shimokawa: Jpn. J. Appl. Phys., 46 (40) (2007) L979-L981.

Exposure dose dependence on line edge roughness of a latent image in electron/extreme ultraviolet lithographies studied by Monte Carlo technique, A. Saeki, T. Kozawa, S. Tagawa, H. B. Cao, H. Deng, M. J. Leeson: J. Micro/Nanolith. MEMS MOEMS, 6 (2007).

Theoretical Study on Relationship between Acid Generation Efficiency and Acid Generator Concentration in Chemically Amplified Extreme Ultraviolet Resists, T. Kozawa, S. Tagawa, M. Shell: Jpn. J. Appl. Phys., 46 (47) (2007) L1143-L1145.

Point Spread Function for the Calculation of Acid Distribution in Chemically Amplified Resists Used for Electron-Beam Lithography, T. Kozawa, S. Tagawa: Jpn. J. Appl. Phys., 46 (48) (2007) L1200-L1202.

Scanning Tunneling Microscopy Profiling of Steep Ridges Using Metal-Coated Carbon Nanotube Tip, Y. Murata, M. Kishida, K. Motoyoshi, T. Kimura, S. Honda, K. Okamoto, Y. Matsui, S. Tagawa, M. Katayama: Jpn. J. Appl. Phys., 46 (12) (2007) 8005-8007.

Sensitization Distance and Acid Generation Efficiency in a Model System of Chemically Amplified Electron Beam Resist with Methacrylate Backbone Polymer, T. Kozawa, S. Tagawa, T. Kai, T. Shimokawa: J. Photopolym. Sci. Technol., 20 (4) (2007) 577-583.

Reactivity between Biphenyl and Precursor of Solvated Electrons in Tetrahydrofuran Measured by Picosecond Pulse Radiolysis in Near-Ultraviolet, Visible, and Infrared, A. Saeki, T. Kozawa, Y. Ohnishi, S. Tagawa: J. Phys. Chem. A, 111 (7) (2007) 1229-1235.

Polymer-Structure Dependence of Acid Generation in Chemically Amplified Extreme Ultraviolet Resists, H. Yamamoto, T. Kozawa, S. Tagawa, H. B. Cao, H. Deng, M. J. Leeson: Jpn. J. Appl. Phys., 46 (7) (2007) L142-L144.

Single-Component Chemically Amplified Resist Based on Dehalogenation of Polymer, H. Yamamoto, T. Kozawa, S. Tagawa, K. Ohmori, M. Sato, H. Komano: Jpn. J. Appl. Phys., 46 (26) (2007) L648-L650.

Study of Acid-Base Equilibrium in Chemically Amplified Resist, K. Natsuda, T.

Kozawa, A. Saeki, K. Okamoto, S. Tagawa, K. Ohmori, M. Sato, H. Komano: Jpn. J. Appl. Phys., 46 (11) (2007) 7285-7289.

Effect of Acid Diffusion and Polymer Structure on Line Edge Roughness, H. Yamamoto, T. Kozawa, A. Saeki, K. Okamoto, S. Tagawa, K. Ohmori, M. Sato, H. Komano: Jpn. J. Appl. Phys., 46 (10) (2007) 6187-6190.

Subpicosecond pulse radiolysis in liquid methyl-substituted benzene derivatives, K. Okamoto, T. Kozawa, A. Saeki, Y. Yoshida, S. Tagawa: Radiat. Phys. Chem., 76 (5) (2007) 818-826.

### **International Conferences**

Dynamics of PHS radical cation (poster), K. Okamoto, T. Kozawa, S. Tagawa: SPIE.

High Precision Measurement of Higher Diffraction-order Contamination in Monochromatized Soft X-ray by using a Compact Transmission-Grafting Spectrometer (poster), K. Fukui, T. Sakai, T. Hatsui, N. Kosugi, Y. Hamamura, K. Okamoto, Y. Matsui, T. Kozawa, S. Seki, S. Tagawa: International Conference on Vacuum Ultraviolet Radiation Physics.

Effect of Fluorine Atom on Acid Generation in Chemically Amplified EUV Resists (poster), H. Yamamoto, T. Kozawa, S. Tagawa, H. Yukawa, M. Sato, H. Komano: EUVL Symposium.

Single-Component Chemically Amplified Resist Based on Dehalogenation of Polymer (poster), H. Yamamoto, T. Kozawa, S. Tagawa, K. Ohmori, M. Sato, H. Komano: SPIE.

Development and Performance of Quasi-Free Standing Transmission-Grating for Soft X-ray Emission Spectrometer (poster), H. Takai, K. Okamoto, M. Matsui, T. Kozawa, S. Seki, S. Tagawa, Y. Hamamura, N. Kosugi: International Conference on Vacuum Ultraviolet Radiation Physics.

Pulse Radiolysis of Polystyrene and Derivatives (invited), K. Okamoto, M. Tanaka, S. Seki, T. Kozawa, S. Tagawa: International Congress of Radiation Research.

Dependence of Absorption Coefficient and Acid Generation Efficiency on Acid Generator Concentration in Chemically Amplified EUV Resist (poster), R. Hirose, T. Kozawa, S. Tagawa, T. Kai, T. Shimokawa: Microprocess and Nanotechnology Conference.

Effect of Fluorine Atom on Acid Generation in Chemically Amplified EUV Resists (poster), H. Yamamoto, T. Kozawa, S. Tagawa, H. Yukawa, M. Sato, J. Onodera: Microprocess and Nanotechnology Conference.

Study on the Reaction of Acid Generators with Epithermal Electrons (poster), K. Natsuda, T. Kozawa, A. Saeki, S. Tagawa, T. Kai, T. Shimokawa: Microprocess and Nanotechnology Conference.



Pico- and Subpico-second Pulse Radiolysis Based on L-band Lnac with Femtosecond White Light Continuum (invited), A. Saeki, T. Kozawa, S. Tagawa: ASR symposium.

Study on Dynamics of Radical Ions of Polystyrenes by Pulse Radiolysis (invited), K. Okamoto, M. Tanaka, T. Kozawa, S. Seki, S. Tagawa: International Congress of Radiation Research.

Dependence of Acid Generation Efficiency on Acid Molecular Structure and Concentration of Acid Generator in Chemically Amplified EUV Resist (poster), R. Hirose, T. Kozawa, S. Tagawa, T. Kai, T. Shimokawa: SPIE.

Acid-Base Equilibrium in Chemically Amplified Resist, K. Natsuda, T. Kozawa, K. Okamoto, S. Tagawa: SPIE.

Monte Carlo Simulation on Line Edge Roughness after Development in Chemically Amplified Resist of Post-optical Lithography, A. Saeki, T. Kozawa, S. Tagawa, H. B. Cao, H. Deng, M. J. Leeson: SPIE.

Reactivity of Pre-solvated Electrons in Tetrahydrofuran Studied by Picosecond Pulse Radiolysis in near-UV to IR (poster), A. Saeki, T. Kozawa, S. Tagawa: Trombay Symposium of Radiation and Photochemistry 2008.

Development of Single Component Chemically Amplified Resist Based on Dehalogenation of Polymer (poster), H. Yamamoto, T. Kozawa, S. Tagawa, K. Ohmori, M. Sato, H. Komano: 11th Sanken International Symposium 6th nanotechnology center international symposium 1st MSTEC international symposium.

Line Edge Roughness in Chemically Amplified Resist of Electron Beam Lithography (poster), A. Saeki, T. Kozawa, S. Tagawa, H. B. Cao: 11th Sanken International Symposium 6th nanotechnology center international symposium 1st MSTEC international symposium.

Study on the Reaction of Acid Generators with Precursor of Solvated Electrons in Tetrahydrofuran (poster), K. Natsuda, T. Kozawa, A. Saeki, S. Tagawa, T. Kai, T. Shimokawa: The International Global COE symposium on Global Education and Bio-Environmental Chemistry(GCOEBEC).

#### **Contributions to International Conferences and Journals**

- |           |                                                                                       |
|-----------|---------------------------------------------------------------------------------------|
| T. Kozawa | 20 th Microprocess and Nanolithograph Conference (Paper Committee)                    |
| T. Kozawa | 2007 International Extreme Ultraviolet Lithography (EUVL) Symposium (Paper Committee) |

#### **Publications in Domestic Meetings**

|                                          |          |
|------------------------------------------|----------|
| The Japan Society of Radiation Chemistry | 5 papers |
| Chemical Society of Japan                | 2 paper  |
| Atomic Energy Society of Japan           | 1 papers |
| The Japan Society of Applied Physics     | 9 papers |
| The Society of Polymer Science, Japan    | 1 paper  |

## Academic Degrees

### Doctor Degree for Engineering

|            |                                                                                                |
|------------|------------------------------------------------------------------------------------------------|
| K. Okamoto | Studies on Primary Processes and Cationic Species Dynamics in Radiation Chemistry of Aromatics |
|------------|------------------------------------------------------------------------------------------------|

## Sponsorships

### Grant-in-Aid for Scientific Research on Priority Areas (S)

|           |                                                                       |             |
|-----------|-----------------------------------------------------------------------|-------------|
| S. Tagawa | Femtosecond Pulse Radiolysis Study on Nano Spatial-temporal Reactions | ¥25,610,000 |
|-----------|-----------------------------------------------------------------------|-------------|

### Grant-in-Aid for Scientific Research on Priority Areas (B)

|           |                                                                                                                                  |            |
|-----------|----------------------------------------------------------------------------------------------------------------------------------|------------|
| T. Kozawa | Nano-space Reaction for Establishment of Academic Basis toward Realization of Ultrafine Fabrication by Extreme Ultraviolet Light | ¥7,410,000 |
|-----------|----------------------------------------------------------------------------------------------------------------------------------|------------|

### Grant-in-Aid for Scientific Research, Encouragement of Young Scientist (B)

|            |                                                                                                                 |            |
|------------|-----------------------------------------------------------------------------------------------------------------|------------|
| K. Okamoto | Elucidation of Molecular Dynamics and Reaction Mechanism for Control of Nano-size Roughness in Resist Materials | ¥1,200,000 |
|------------|-----------------------------------------------------------------------------------------------------------------|------------|

### Entrusted Research

|           |             |                                                                                    |             |
|-----------|-------------|------------------------------------------------------------------------------------|-------------|
| S. Tagawa | JST-CREST   | Research on Resist for Ultra-fine Fabrication and Development of Process Simulator | ¥26,910,000 |
| S. Tagawa | Intel Corp. | Nanoscale Distribution of Acid in Chemically Amplified EUV Resists                 | ¥13,962,000 |
| S. Tagawa | ASET        | Research on Reaction Mechanism of Chemically Amplified Resist                      | ¥1,000,000  |

### Other Research Fund

|           |                                    |                                                |            |
|-----------|------------------------------------|------------------------------------------------|------------|
| S. Tagawa | Mitsubishi gas chemical company    | Basic Study on ArF Photo Resist                | ¥500,000   |
| S. Tagawa | SELETE                             | Research on EUV Resist                         | ¥500,000   |
| S. Tagawa | Matsushita Electric Industrial Co. | Dissolution Property of EUV Lithography Resist | ¥1,000,000 |

## Department of Ultrafast Spectroscopy of Nanostructures

Visiting Research Scholar: Ivo Frébort (2007.4.3–2007.5.14)

### Outlines

Aminohydrolases adenine deaminase (ADE, EC 3.5.4.2; catalyzing irreversible deamination of adenine to hypoxanthine) and adenosine deaminase (ADA, EC 3.5.4.4; catalyzing irreversible deamination of adenosine to inosine) are enzymes that are responsible for metabolic salvage of purine compounds. Several subclasses of these enzymes have been already described and with the recent knowledge of full genome sequences of many organisms, it is possible to identify encoding genes and group the enzymes according to primary structure. We focused on the enzymes of yeast and plant origin that have not been previously isolated and characterized.

### Achievement

Homogeneous adenine deaminases from yeasts *Saccharomyces cerevisiae* and *Schizosaccharomyces pombe* and adenosine deaminase from *Arabidopsis thaliana* were obtained for the first time as recombinant proteins by molecular cloning of the corresponding genes and overexpressing them in *Escherichia coli*. The enzymes showed comparable molecular properties to well known mammalian adenosine deaminases, but exhibited much lower  $k_{\text{cat}}$  values. Adenine and adenosine were the best substrates for the yeast and plant enzyme, respectively. Interestingly, one of the enzymes also exhibited significant activity towards  $N^6$ -substituted adenines that are commonly known as plant hormones cytokinins and their synthetic derivatives used for cancer therapy or as cosmetics. The activity towards these compounds was subsequently found also for commercial preparation of human adenosine deaminase (ADA1). Our results show that these enzymes may be affecting the level of exogenously applied compounds and thus compromise their physiological or therapeutic effect.

Structural characterization of the enzymes is a current issue as only the structure of mammalian ADA is known, which shares less than 25% protein sequence identity with the yeast and plant enzymes. In preliminary screening, small crystals have been obtained for all three proteins. Further experiments are in progress to grow larger crystals suitable for structural analysis that is the ultimate goal of our collaboration.

## Department of Ultrafast Spectroscopy of Nanostructures

Visiting Research Scholar: Patrick Henry TOY (2007.5.16-2007.6.28)

### Outlines

The aim of this research is the creation of “superenzyme” which is expected to show an excellent catalytic activity in addition to the high enantioselectivity as natural enzymes exhibit. To accomplish the purpose, we plan to utilize the harmony of two different sites: one is a “recognition site” where substrates are precisely controlled to display high selectivity, the other is a “reaction site” which promotes reactions with high efficiency. We have developed a new methodology for the incorporation of multifunctional asymmetric catalysts as a recognition site and spherical nanoparticles as a reaction site into one molecule.

### Achievement

Efficient immobilization of BINOL moieties onto the surface of a micelle-derived spherical nanoparticle was achieved. Taking advantage of the facile adsorption of thiols to the surface of gold cluster, the disulfide bearing BINOL moieties at each terminal position was successfully introduced on monolayer-protected metal cluster (MPC). It was found that Ti-BINOLate complexes generated from such nanoparticles efficiently promoted catalytic asymmetric reactions (alkylation of benzaldehyde and Michael reaction of 2-cyclohexen-1-one) to afford the corresponding adducts with excellent selectivity.

## **Department of Ultrafast Spectroscopy of Nanostructures**

Guest Professor: Ayyappanpillai Ajayaghosh (2007.6.29-2007.7.31)

### **Outlines**

The purpose of this project is molecular structure design and synthetic route design of conjugated oligomeric compounds with high self-aggregation properties forming organic gels and nano-wires. These nanostructures are expected to possess promising electronic properties for organic electronics.

### **Achievement**

Control of supramolecular organization of chromophores plays a key role in facilitating electron and energy transfer process, which are extremely important to the design of organic materials for electronics. We have tried an approach of the gelation of molecules, which is known to facilitate the formation of supramolecular architectures of nanometer to micrometer dimensions of different shape and morphology. Self-assembly and gelation of linearly pi-conjugated molecules allow significant modulation of their optoelectronic properties. We have investigated the molecular structure design and synthetic route design of functionalized oligothiophenes forming entangled nanostructures via the cooperative interactions of H-bonding, pi-pi stacking, and van der Waals forces.

The following two lectures have been also held.

" Molecular Self-assemblies as Scaffolds for Excitation Energy Transfer ", July 4, 2007.

" Squaraine Dyes: Versatile Chromophores for the Design of Cation Probes and Nanoarchitectures ", July 10, 2007.

## **Department of Ultrafast Spectroscopy of Nanostructures**

Visiting Research Scholar: Jiang Yu ZHENG (2007.8.1-2007.8.31)

### **Outlines**

A life log platform is effective to constantly record personal experiences and events in our daily life and to retrieve the recorded images when needed. We develop a method for efficient browsing in which a wearable omnidirectional camera system is applied to record the daily personal experiences and events.

### **Achievement**

First we considered the basic design of the wearable omnidirectional camera system as a method to optically record life logs.

Recorded images are then sorted in order by time, space and events. We showed an image summary method for efficient browsing. In this method, we divided the images into background, near objects and moving objects in order to obtain spatio-temporal summary. As a result, we can simultaneously view multiple events. It has also become possible to get even more global information by sharing optical images from others' point of view.

## **Department of Ultrafast Spectroscopy of Nanostructure**

Visiting Associate Professor: Pradeep K. Pujari (2007.9.3-2007.12.3)

### **Outlines**

Dr. P.K.Pujari is an Indian researcher belonging to Bhabha Atomic Research Center in India and stayed from September to December in 2007 as a visiting associate professor in Nanoscience and Nanotechnology Center of ISIR. His research field is material science, especially polymer science, by using radioisotope (RI) based positron annihilation spectroscopy (PAS). Recently he started developing a slow positron beam facility based on RI in his laboratory. He has been promoting research works powerfully. The purpose of this stay in ISIR was joining the research works relating to the analysis of polymer electrolyte membrane (PEM) with positron and the construction of slow positron beamline organized by the group of Advanced Quantum Beams. His group had made pioneer works about PEM using positron, so the collaboration was expected to be valuable. During his stay, he had joined several experiments regarding to not only positron but also FTIR, ESR to investigate what is happened in PEM exposed to  $\gamma$ -ray. He had mainly been engaged in the data analysis brought from those techniques, especially ESR, and his contribution to others was great. The results were presented in the meeting of positron society, which was held in Reactor Institute of Kyoto University in November. He also gave a lecture about his recent works relating to the analysis of frozen process of water in nano-scale pour using PAS technique and fruitfull discussion was made among attendee.

## Department of High Speed Nanostructures

Visiting Research Scholar: Hossain Akther Kashem Mohammad (2007.12.4-2008.1.31)

### Outlines

Iron oxide  $\text{Pb}(\text{Fe}, \text{Ta})_{0.5}\text{O}_3$  and  $\text{Ba}(\text{Fe}, \text{Ta})_{0.5}\text{O}_3$  that has the perovskite type structure is an interesting material that shows ferromagnetism and strong dielectric according to the double exchange interaction between iron B sites. However, it is a current state that most is unclarification as for the ferromagnetism and strong dielectric interrelation and a physical origin. Then, the above-mentioned perovskite type iron oxide was synthesized by the solid reaction method, the magnetism and permittivity were measured, and the ferromagnetism, strong dielectric characteristic, and the coupling were examined.



## Department of Ultrafast Spectroscopy of Nanostructures

Visiting Research Scholar: Asuha (2008.2.1-2008.3.31)

### Outlines

Semiconductor elements form the backbone of electronic devices which are indispensable for the modern society. Properties of both ultra-thin insulator films/semiconductor interfaces and dielectric films greatly affect device characteristics and thus, studies on these physical properties are important in both basic and applied researches. We have focused on formation and characterization of insulating films in thin film transistors (TFT) for liquid crystal display (LCD).

### Achievement

Polycrystalline Si (poly-Si) surfaces were oxidized in an apparatus for nitric acid oxidation of poly-Si deposited on glass substrates with  $30 \times 42 \text{ cm}^2$  in size for TFT use. The thickness of  $\text{SiO}_2$  thin films was  $\sim 1 \text{ nm}$ , and the dispersion was less than 5%. X-ray photoelectron spectroscopy (XPS) showed very small amount of defects in the  $\text{SiO}_2$  films and at the  $\text{SiO}_2$ -Si interfaces. A p-Si(100) wafer oxidized with TFT samples at the same time was used for electrical characterization. Al electrodes were deposited on the Si wafer to form  $\langle \text{Al/SiO}_2/\text{Si}(100) \rangle$  MOS diode structures. Current-voltage measurements indicated that, after annealing under  $\text{H}_2$  atmosphere (PMA, post metallization annealing), the  $\text{SiO}_2$  film formed by nitric acid oxidation gave a lower leakage current density than that of thermal oxide films. Capacitance-voltage measurements showed PMA decreased interface states. This indicated that H atoms terminated Si dangling bonds at the  $\text{SiO}_2$ -Si interface.

### Publications

#### Original Papers

S. Mizushima, S. Imai, Asuha, M. Tanaka, and H. Kobayashi, Nitric acid method for fabrication of gate oxides in TFT, Appl. Surf. Sci. 254, 3685-3689 (2008).

#### International Conferences

H. Kobayashi, Asuha, T. matsumoto and M. Takahashi, Nitric Acid Oxidation of Si and SiC for the Low Temperature Fabrication of MOS Structure, Interntional Seminar on Semiconductor Surface Passivation 2007.

T. Matsumoto, Asuha, Y.-L. Liu, S. Imai, S. Mizushima, M. Takahshi, and H. Kobayashi, Nitric Acid Oxidation of Si (NAOS) and Defect Passivation Etch-Less Cleaning (DPEL) Method to Improve Si Devices, 3rd Handai Nano Symposium.

# Division of Nanoscience and Nanotechnology for Industrial Applications

## Outline

This division involves five laboratories, i.e., Department of Nanomaterials and Environmentally Conscious Technology, Department of Computational Nanomaterials Design, Department of Nano-Bio-Intelligent Systems Science, Department of Propatent Strategy for Nanotechnology (Domestic visiting researcher), Department of Nanotechnology Transfer (Foreign visiting researcher). All of these laboratories have the same direction to make contribution to society and industries through their own nanotechnology. Through the activity of these laboratories in the first year, establishments are listed as follows.

## Achievements

### Suganuma Lab.

- Establishment of basic design and science of high temperature lead-free soldering
- Understanding of basic mechanism of tin whisker formation
- Development of Printed Electronics technology with nano particles paste
- Basic design of high reliability conductive adhesives and evaluation methods

### Mizoguchi Lab.

- Development of a design supporting system for nano-materials based on ontology engineering
- Development of contents management system based on nanotechnology ontology
- Refinement of nanotechnology ontology based on an ontological consideration of function and quality
- Augmentation of Hozo for construction of a medical ontology
- Development of an advanced database for life science based on ontology engineering

### Katayama-Yoshida Lab.

- Development of materials design engine and materials design for semiconductor spintronics
- Development of pseudopotential electronic-structure calculation codes “Osaka2002\_nano”
- Superconductivity research by doped semiconductors
- Material design for impurity control in semiconductors
-

## **Department of Nanomaterials and Environmentally Conscious Technology**

Professor: Katsuaki SUGANUMA  
Assistant Professor: Masahiro INOUE, Keun-Soo KIM (2007.10.16~)  
Post Doctoral Fellows: Do-Seop KIM, Sun-Sik KIM, Jinting JIU, Keiichi MURAI  
Graduate Students: Seiji KUMAMOTO, Gorou IZUTA, Mitsuru KAWAZOME,  
Masafumi KURAMOTO, Daisuke WAKUDA,  
Seong-Jun KIM, ALONGHENG, Min Kang  
Research Student: Chang-Jae KIM (2007.5.1-2008.3.31)  
Support Staff: Mariko HATAMURA, Hiroo HIGUCHI,  
Noriko KAGAMI, Kyoko HAMASAKI, Kozue IDE,  
Misa MATSUSHITA.

### **Outlines**

Through nanotechnologies and knowledge for organic/inorganic materials, we are conducting the development of environmentally conscious fine technologies for electronics packaging area, i.e., lead-free soldering and conductive adhesives, and the composite materials based on metals and intermetallic compounds. We set our route towards contributions to our society in near future.

### **Current Research Project**

#### **Development of alternative technology for high-temperature soldering**

Isotropic conductive adhesives have excellent attributes as heat-resistant lead-free high temperature interconnection materials as well as those enabling low temperature manufacturing of circuits. Ag metallic particles from nano-scale to micron-scale are combined with organic matrix to provide sound high-temperature lead-free interconnection. The purpose of the project is to understand the current characteristics of conductive adhesives as the alternative to leaded solders, and, especially focusing on their characteristics of high temperature resistance and of low temperature manufacturing process, new conductive adhesives are targeted to be developed by the improvement of the current drawbacks.

#### **Development of new room temperature wiring method for Printed electronics**

Room temperature wiring is one of the last goals for Printed Electronics. Room temperature fabrication enables to use the wide variety of functional materials into one circuit board without thermal stress or damage as well as environmental consciousness. Metallic nanoparticles can be sintered to form dense microstructure if both the surface of nanoparticles and the environment are clean without any oxidation or contamination. Ag nanoparticles are, however, usually protected by an organic layer. It is desirable to remove this organic layer by certain chemical processes with or without light heating or other kinds of energy processes, which do not have any serious damage on organic devices and substrate weak against heating. Recently, we developed a new process, by

which the paste of Ag nanoparticles protected with them can be successfully sintered at room temperature in air atmosphere.

### **Development of soft human/machine interfaces using super-flexible wiring technology**

Recently, the super-flexible (bendy and stretchable) wiring technology using elastomer-based conductive adhesives was developed in our group. By using the super-flexible wiring, stretchable tactile sensor systems including piezoelectric sensor and novel electrostatic sensor systems for humanoid robots and related applications were successfully fabricated. In addition, these sensor systems were connected to a self-organized network of distributed processors in order to realize the fail-safe data processing system and shown to work successfully.

## **Publications**

### **Original Papers**

A super-flexible sensor system for humanoid robots and related applications, M. Inoue, Y. Kawahito, Y. Tada, T. Hondo, T. Kawasaki, K. Suganuma, H. Ishiguro: Journal of Japan Institute of Electronics Packaging, 11 (2) (2008) 136-140.

Structures and purification of boron nitride nanotubes synthesized from boron-based powders with iron particles, N. Koi, T. Oku, M. Inoue, K. Suganuma: J. Materials Science, 43 (8) (2008) 2955-2961.

Effects of Ag and Cu addition on microstructural properties and oxidation resistance of Sn-Zn eutectic alloy, J.E. Lee, K.S. Kim, M. Inoue, J. Jiang, K. Suganuma: J. Alloys and Compounds, 454 (1-2) (2008) 310-320.

A study on solder electromigration in Cu/In/Cu flip-chip joint system, K. Yamanaka, Y. Tsukada, K. Suganuma: Journal of Japan Institute of Electronics Packaging, 11 (1) (2008) 60-65.

Thermal stability of poly(vinylidene fluoride) films pre-annealed at various temperatures, M. Inoue, Y. Tada, K. Suganuma, H. Ishiguro: Polymer Degradation and Stability, 92 (10) (2007) 1833-1840.

The dependence on thermal history of the electrical properties of an epoxy-based isotropic conductive adhesive, M. Inoue, K. Suganuma: J. Electronic Materials, 36 (6) (2008) 669-675.

Development of an electronic packaging technique using conductive adhesives for novel human-machine interfaces, M. Inoue, H. Sasaki, K. Suganuma, T. Kawasaki, T. Rokuhara, T. Miyashita, H. Ishiguro: Advances in Technology of Materials and Materials Processing Journal, 9 (1) (2007) 49-54.

Novel method for room temperature sintering of Ag nanoparticle paste in air, D.

Wakuda, M. Hatamura, K. Suganuma: Chemical Physics Letters, 441 (4-6) (2008) 305-308.

Formation and atomic structure of boron nitride nanotubes with a cup-stacked structure, T. Oku, N. Koi, K. Suganuma, R.V. Belosludov, Y. Kawazoe: Solid State Communications, 143 (6-7) (2007) 331-336.

Formation and atomic structures of boron nitride nanotubes with cup-stacked and Fe nanowire encapsulated structures, T. Oku, N. Koi, I. Narita, K. Suganuma: Materials Transactions, 48 (4) (2007) 722-729.

Thermal properties and phase stability of Zn-Sn and Zn-In alloys as high temperature lead-free solder, J.E. Lee, K.S. Kim, K. Suganuma, M. Inoue, G. Izuta: Materials Transactions, 48 (3) (2007) 584-593.

Process development and application of noble metal nanoparticle related materials by total eco-design, Y. Hayashi, D. Ishikawa, H. Takizawa, M. Inoue, K. Suganuma, K. Niihara: Journal of the Japan Society of Powder and Powder Metallurgy, 54 (3) (2007) 186-193.

### **Review Papers**

Printed electronics new trends for conductive adhesives solder alternatives and printed electronics, K. Suganuma, J. Adhesion Society of Japan, vol. 43-5 (2007) 220-224.

Development of High Temperature Lead-Free Solder and Their Reliability Evaluation, J.E. Lee, K.S. Kim, K. Suganuma, Y.G. Jung, Trends in Metals & Materials Engineering, vol. 20-3 (2007) 30-39.

Process development and application of noble metal nanoparticle related materials by total eco-design, Y. Hayashi, D. Ishikawa, H. Takizawa, M. Inoue, K. Suganuma, K. Niihara, Powder and Powder Metallurgy, vol.54-3 (2007) 186-193.

### **Books**

Ink-jet Wiring of Fine Pitch Circuits with Metallic Nano Particle Inks, Applications & Materials of Inkjet Printer II (In Japanese, ed. by K. Takahashi), K. Suganuma, D. Wakuda, K. S. Kim, CMC Publications, (2007) 209-218.

Handbook of Lead-Free Soldering Technology and Materials (In Japanese), K. Suganuma (editor), Kogyo Chosakai Publishing, Inc.

### **Patents**

Method for forming wirings on substrates by sintering using coated metal nanoparticles, K. Suganuma, D. Wakuta, M. Hatamura, JP 2008-72052.

Solder alloys and soldering process, G. Izuta, K. Hiraoka, K. Suganuma, JP 2007-275921.

Manufacture of conductive elastic rubber materials provided with series-connected conductive particles, K. Suganuma, M. Inoue, H. Ishiguro, T. Kawasaki, T. Rokuhara, T. Miyashita, JP 2007-173226.

### **International Conferences**

Interfacial Reactions of Die Attached AlN-DBC Module Using Zn-Sn High Temperature Solders (poster), S.J. Kim, K.S. Kim, D.S. Kim and K. Suganuma: 137th TMS Annual Meeting & Exhibition, New Orleans, LA, USA, Mar.9-Mar.13, 2008.

Degradation of Ag-Epoxy Conductive Adhesive/Sn Interface in Humid Atmosphere (invited), S.S. Kim, K.S. Kim and K. Suganuma: 137th TMS Annual Meeting & Exhibition, New Orleans, LA, USA, Mar.9-Mar.13, 2008.

Room Temperature Sintering of Ag Nanoparticle Paste and its Mechanism (poster), D. Wakuda, M. Hatamura and K. Suganuma: MRS Fall Meeting, Boston, MA, USA, Nov. 26-30, 2007.

Zn-Sn and Zn-In high temperature lead-free solders (poster), K. Suganuma, S.J. Kim, J.E. Lee, K.S. Kim,: 40th International Symposium on Microelectronics (IMAPS2007), McEnery Convention Center, San Jose, California USA, Nov. 11-15, 2007.

Impact property evaluation of Ag-epoxy conductive adhesive joint (poster), D.S. Kim, M. Kang, K.S. Kim, S.S. Kim, S.J. Kim, K. Suganuma: 40th International Symposium on Microelectronics (IMAPS2007), McEnery Convention Center, San Jose, California USA, Nov. 11-15, 2007.

Design and synthesis of mesoporous nano-silver-based die attach material for high power electronics (poster), K. Suganuma, J. Jiu, D.S. Kim, K.S. Kim: 40th International Symposium on Microelectronics (IMAPS2007), McEnery Convention Center, San Jose, California USA, Nov. 11-15, 2007.

Ink-jet printing of Nano Materials and Process for Electronics Applications (poster), K. Suganuma, D. Wakuda, M. Hatamura, K.S. Kim,: 9th International IEEE CPMT Symposium on High Density Design, Packaging and Microsystem Integration (HDP' 07), Shanghai, China, Jun. 26-28, 2007.

A super-flexible sensor system for humanoid robots and related applications, M. Inoue, Y. Kawahito, Y. Tada, T. Hondo, T. Kawasaki, K. Suganuma, H. Ishiguro,: International Conference on Electronics Packaging (ICEP) 2007, Tokyo, Japan, April, 2007.

Temperature dependence of electrical resistivity of isotropic conductive adhesive composed of an epoxy-based binder (invited), M. Inoue, H. Muta, S. Yamanaka, K. Suganuma: 9th International IEEE CPMT Symposium on High Density Design, Packaging and Microsystem Integration (HDP' 07), Shanghai, China, Jun. 26-28, 2007.

A Flexible and Stretchable Tactile Sensor Utilizing Static Electricity, Y. Tada, M. Inoue, T. Kawasaki, Y. Kawahito, H. Ishiguro, K. Suganuma: the 2007 IEEE/RSJ International Conference on Intelligent Robots and Systems.

### **Contributions to International Conferences and Journals**

|             |                                                                                                                             |
|-------------|-----------------------------------------------------------------------------------------------------------------------------|
| K. Suganuma | TMS Annual Meeting Committee of Phase Stability, Phase Transformation, and Reactive Phase Formation in Electronic Materials |
| K. Suganuma | Electronic Components and Technology Conference (ECTC), Materials Processing Committee                                      |

### **Publications in Domestic Meetings**

|                                          |          |
|------------------------------------------|----------|
| Japan Institute of Electronics Packaging | 4 papers |
| Japan Institute of Metals                | 2 papers |

### **Academic Degrees**

#### **Master Degree for Engineering**

|           |                                                               |
|-----------|---------------------------------------------------------------|
| Alongheng | Effect of Reflow Atmosphere on Sn-Ag-Cu soldering Reliability |
|-----------|---------------------------------------------------------------|

### **Sponsorship**

#### **Grant-in-Aid for Scientific Research on Priority Areas**

##### **Grant-in-Aid for Scientific Research (A)**

|             |                                                                                                          |            |
|-------------|----------------------------------------------------------------------------------------------------------|------------|
| K. Suganuma | Establishment of bases for synthesis of metal nano-particles and for wiring technology using nano-pastes | ¥5,720,000 |
|-------------|----------------------------------------------------------------------------------------------------------|------------|

#### **Grant-in-Aid for Scientific Research (\*) (\*)**

#### **Grant-in-Aid for Scientific Research on Exploratory Research**

##### **Entrusted Research**

|             |              |                                                                      |             |
|-------------|--------------|----------------------------------------------------------------------|-------------|
| K. Suganuma | NEDO         | Development of alternative technology for high-temperature soldering | ¥23,800,000 |
| K. Suganuma | Research and | Development of hybrid Ag                                             | ¥14,700,000 |

|                            |                                                     |                                                                      |            |
|----------------------------|-----------------------------------------------------|----------------------------------------------------------------------|------------|
|                            | Development Association for Future Electron Devices | nano-pastes applicable for SiC device packaging                      |            |
| K. Suganuma                | NEC Co. Ltd.                                        | Development of interconnecting technology using conductive Adhesives | ¥1,050,000 |
| <b>Other Research Fund</b> |                                                     |                                                                      |            |
| K. Suganuma                | Mitsubishi Chemical Co.                             |                                                                      | ¥6,562,000 |
| K. Suganuma                | Mitsubishi Electric Co.                             |                                                                      | ¥6,000,000 |
| K. Suganuma                | Teijin Ltd.                                         |                                                                      | ¥1,200,000 |
| K. Suganuma                | Toppan Forms Co. Ltd.                               |                                                                      | ¥3,000,000 |
| K. Suganuma                | Okuno Chemical Industries Co. Ltd.                  |                                                                      | ¥2,000,000 |
| K. Suganuma                | AIR LIQUIDE LABORATORIES                            |                                                                      | ¥1,500,000 |
| K. Suganuma                | Toray Engineering Co. Ltd.                          |                                                                      | ¥1,000,000 |
| K. Suganuma                | NOF Co.                                             |                                                                      | ¥900,000   |
| K. Suganuma                | Bando Chemical Industries, Ltd.                     |                                                                      | ¥500,000   |
| K. Suganuma                | UBE-NITTO KASEI Co. LTD.                            |                                                                      | ¥450,000   |



## Department of Computational Nanomaterials Design

Professor: Hiroshi KATAYAMA-YOSHIDA  
Associate Professor: Koun SHIRAI  
Research Associate: Kazunori SATO  
Post Doctoral Fellows: Van An DINH, Ikutaro HAMADA, Susumu YANAGISAWA  
Graduate Students: Hidetoshi KIZAKI, Masayuki TOYODA,  
Tetsuya FUKUSHIMA, Hideki HAYASHIDA,  
Kenji TOYODA, Haruhiko DEKURA, Kunihiro HARADA,  
Motohiko ETO, Yousuke NAKANO,  
Hironobu YAMAGUCHI, Akihumi UOZUMI,  
Hideyuki JIPPOU, Jun ISHISADA, Hitoshi FUJII  
Under Graduate Students: Yuki TERATANI, Ryusuke TOMINAGA  
Supporting Staff: Mika ASADA, Ryoko ITO

### Outlines

The primary activities of this department are theoretical study of electronic properties of nanomaterials, which are different from those of bulk crystals. The first-principles calculations based on the density-functional theory are used, in order to exclude any empirical parameters. More importantly, we wish to predict unknown features of new nanostructure and design novel nanomaterials. Lead of the area of material research from the theoretical viewpoint is one of our goals.

At the same time, efforts are continued to keep development in the methodologies in order to solve difficult problems encountered in this field, because nanoscience is different from study of bulk materials with many respects.

### Current Research Project

#### Development of Pseudopotential Electronic-structure Calculation Codes “Osaka2002\_nano”

Improvement and extension of our developed first-principles calculation code ‘Osaka2002\_nano’ have been in progress. In particular, in this year, improvements have been made on frozen-phonon calculation. The previous version was able to calculate zone-center phonons. But, full dispersions over the zone were not obtained without further involved processing on the obtained data. By using supercell and by constructing the real-space force constants, it is able to calculate full dispersion of phonons. This calculation is useful to identify impurities and even to design doping processes.

#### Material Design for Superconductivity of Icosahedron-based Boron

Growing interests are addressed to solid boron and its compounds because of its superconducting transition at high pressures. Among the variety of polymorphs of boron,  $\alpha$ -boron is particularly interesting, because of its high potentiality of superconductivity. A problem of  $\alpha$ -boron is difficulty in obtaining good-quality crystals. We find a promising path for synthesizing  $\alpha$ -boron with good quality, based on our theoretical

prediction on the phase diagram of boron solids. Furthermore, an effective method of doping on  $\alpha$ -boron has been found. The method is combination of use of Li impurity and high-pressure processing.

### **Simulation of IR excitations for controlling impurities**

Recently, in order to achieve selective diffusion of impurity atoms in silicon, use of excitations of the local vibration mode of impurities attracts much attention in the industrial researches. IR laser is such a means to excite local vibration modes. The experimental setup for examining this effect was been designed by first-principles MD simulation. Based on this MD simulation, IR beam line of Spring-8 is chosen as an intensive IR light source. Now, the experiment is in progress.

### **Mechanism of fast diffusion of Cu impurity in Si**

A distinguishing property of copper impurities in silicon is their very fast diffusivity, which is clearly undesirable in silicon device processes. However, even the stable site of Cu is controversial issue. Most of the researchers of this field believe that the stable site of Cu is tetrahedral interstitial site. However, our study on the formation energy shows that the substitutional site exhibits the same stability as the interstitial site. This may have significant consequences on interpretations various behaviors of Cu.

### **Elastic softening of Crystal Si due to vacancy**

In the silicon device process, there is a strong demand for eliminating copper contamination. Gettering of Cu by dopant atoms is a useful method for this purpose. The gettering of Cu by dopant atoms is studied by Osaka2k. We have assessed the efficiency of gettering through the evaluation of the binding energies between Cu and variety of impurities and their complexes. Based on these calculations, it is found that a BO complex has an outstanding efficiency for the Cu gettering.

### **Microscopic Roles of Hydrogen in Crystal Si**

In bulk silicon grown by Czochralski method, there is a part of vacancy-rich layer. It is difficult to quantitatively estimate the concentration of vacancy, which is an industrial problem to date. Recent discovery of elastic softening by ultrasonic measurement has potential to solve this problem. However, there is no consensus regarding the mechanism of softening. Low-energy excitation must be present in order to have the temperature dependence of softening observed experimentally. A low-excitation has been found in phonon spectra at low temperatures by MD simulation. The may provide a light on the mechanism.

### **Spinodal decomposition and super-paramagnetism in dilute magnetic semiconductors**

Recently, spintronics represents a new paradigm of electronics that utilizes both the electron charge as well as the electron spin degrees of freedom. It has a potential to fabricate new devices which can store and process information simultaneously. One of the critical steps in realizing the spintronics is the fabrication of dilute magnetic semiconductors (DMS) which have high transition temperature. In this year, we have developed materials design engine and applied it to materials design for semiconductor spintronics.

Owing to the recent development of the FP method for calculating magnetic properties of DMS, it has been recognized that the magnetic percolation effect is disastrous to the high temperature ferromagnetism in DMS in particular for low concentrations. The exchange interactions calculated from first-principles are strong for nearest neighbors, but those interactions are short ranged and can not play an important role for realizing high- $T_c$  because the solubility of magnetic impurities into DMS is too low to achieve magnetic percolation.

To overcome this difficulty and realize room temperature ferromagnetism, we focus on the spinodal decomposition in DMS, and suggest that by controlling the spinodal decomposition high blocking temperature can be realized leading to ferromagnetic behaviour at high temperature. We calculate electronic structure of DMS from first-principles by using the Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA) method. We use MACHIKANNEYAMA2002 package developed by Akai. The chemical pair interactions and magnetic exchange interactions between magnetic are calculated for (Ga, Mn)N DMS. Then, we use the Monte Carlo techniques to simulate spinodal decomposition of DMS and to estimate the magnetic properties of them. The computer simulations for the magnetization process of the decomposition phases indicate that we can control super-paramagnetic blocking temperature by optimizing the size of the clusters by changing the crystal growth condition. This simulation suggests the material design of high blocking temperature DMS by controlling the spinodal decomposition.

In general, DMS systems have solubility gap and favors phase separation, therefore, the similar effect can be expected for the other DMS systems. The process of the spinodal decomposition depends sensitively on the crystal growth condition, therefore the present simulation also explains large scattering of the experimental  $T_C$ 's of wide band-gap DMS. By our calculations it is also shown that the position and the shape of nano-clusters are controllable by changing the growth condition of the DMS.

### **Design of spintronics materials based on half Heusler alloys**

The prediction and development of new half-metallic ferromagnets are necessary for exploiting the great potentials of spintronics. We propose a new class of high- $T_C$  half-heusler ferromagnets NiMnZ (Z = Si, P, Ge, As). The structural and magnetic properties are investigated through the calculation of the electronic structure, phase stability, equilibrium lattice constant, magnetic exchange interaction and Curie temperature. It is found that all alloys show half-metallicity and ferromagnetism at temperature much higher than room temperature in a wide range of lattice expansion. At the equilibrium lattice constant,  $T_C$  of 715, 840, 875 and 1050 K are predicted by Monte Carlo simulation for NiMnP, NiMnAs, NiMnGe and NiMnSi, respectively. Following these results, these alloys are strongly expected to be promising candidates for spintronic applications. We also investigated Mn-doped half-Heusler type DMS systems, such as Fe(V, Mn)Sb, Co(Ti, Mn)Sb, Ni(Ti, Mn)Sn and Ni(Zr, Mn)Sn. It is found that Mn-doped CoTiSb and NiTiSn systems have room temperature ferromagnetism for high Mn concentrations of 25 to 30 %.

### **Design of co-doping method in DMS**

We propose co-doping method for increasing solubility of magnetic impurities in dilute magnetic semiconductors (DMS). The concentration dependences of the mixing

energy of DMS, such as (Ga, Mn)N, (Ga, Cr)N, (Ga, Mn)As and (Zn, Cr)Te, show large convexity and these systems have a tendency toward spinodal decomposition. By introducing compensating impurities into these DMS, it is found that the mixing energy shows gradual transition from convex to concave concentration dependence resulting in negative mixing energy of magnetic impurities. This result suggests that the co-doping method dramatically increases the solubility of magnetic impurities in DMS, thus high concentration doping of magnetic impurities into DMS becomes possible.

The co-doped impurities kill the ferromagnetism of DMS, but they can be removed out by a thermal treatment after crystal growth. We propose interstitials such as Hydrogen as a recommended co-dopant. Recently, Kuroda et al. demonstrated the effect of the co-doping in (Zn, Cr)Te with I and N. Available concentration of the co-dopant in the experiment was so low that the interpretation of the experimental results from the co-doping point of view is prohibited. Further experimental confirmation and theoretical materials design is required.

### **Materials design for colossal thermoelectric cooling power**

In addition to the conventional Peltier effect, we propose a new class of thermoelectric-cooling mechanism based on the adiabatic spin-entropy expansion in a quasi-one-dimensional nano-superstructure by injecting the spin current from the ferromagnetic metal to paramagnetic one. The spin-entropy expansion mechanism dominates and enhances the thermoelectric-cooling power dramatically in current perpendicular to plane-giant magneto-resistance (CPP-GMR) Co/Au nano-interface. Based upon the spin-entropy expansion mechanism, we design the new thermoelectric-cooling nano-superstructures using the newly designed half-Heusler ferromagnets NiMnSi ( $T_C=1050$  K) and self-organized quasi-one-dimensional Konbu-phase (Zn,Cr)Te with very high blocking temperature ( $>1000$  K) by spinodal nano-decomposition.

## **Publications**

### **Original Papers**

Theory of ferromagnetic semiconductors, H. Katayama-Yoshida, K. Sato, T. Fukushima, M. Toyoda, H. Kizaki, V. A. Dinh and P. H. Dederichs: Phys. Stat Solidi a, 204 (2007) 15-32.

First-principles study on the ferromagnetism and Curie temperature of Mn-doped AlX and InX (X = N, P, As and Sb), K. Sato, P. H. Dederichs and H. Katayama-Yoshida: J. Phys. Soc. Jpn., 76 (2007) 24717 (12pp).

Computational nano-materials design for high- $T_C$  ferromagnetism in wide-gap magnetic semiconductors, H. Katayama-Yoshida, K. Sato, T. Fukushima, M. Toyoda, H. Kizaki, V. A. Dinh and P. H. Dederichs: J. Magn. Magn. Mater., 310 (2007) 2070-2077.

Ab initio materials design for transparent conducting oxide based new functional materials, H. Katayama-Yoshida, K. Sato, H. Kizaki, H. Funashima, I. Hamada, T. Fukushima, V. A. Dinh, M. Toyoda: Appl. Phys. A, 89 (2007) 19-27.

Super-paramagnetic blocking phenomena and room-temperature ferromagnetism in wide band-gap dilute magnetic semiconductor (Ga, Mn)N, K. Sato, T. Fukushima and H. Katayama-Yoshida: Jpn. J. Appl. Phys., 46 (2007) L682-L684.

Ferromagnetism and spinodal decomposition in dilute magnetic nitride semiconductors, K. Sato, T. Fukushima, H. Katayama-Yoshida: J. Phys. Condens. Matter, 19 (2007) 365121 (8pp).

Dilute magnetic semiconductors based on half-Heusler alloys, T. Fukushima, K. Sato, H. Katayama-Yoshida and P. H. Dederichs: J. Phys. Soc. Jpn., 76 (2007) 94713-1-5.

Computational nano-materials design for colossal thermoelectric-cooling power by adiabatic spin-entropy expansion in nano-superstructures, H. Katayama-Yoshida, T. Fukushima, V. A. Dinh and K. Sato: Jpn. J. Appl. Phys., 46 (2007) L777-L779.

Trends of exchange interactions in dilute magnetic semiconductors, B. Belhadji, L. Bergqvist, R. Zeller, P. H. Dederichs, K. Sato and H. Katayama-Yoshida: J. Phys. Condens. Matter, 19 (2007) 436227 (12pp).

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Design of colossal solubility of magnetic impurities for semiconductor spintronics by the co-doping method, K. Sato and H. Katayama-Yoshida: Jpn. J. Appl. Phys., 46 (2007) L1120-L1122.

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### **Patents**

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“II-VI group compound based single crystal ferromagnetic compound and method for adjusting its ferromagnetic characteristics”, H. Yoshida, K. Sato Japanese patent No.3998425

“Magnetoresistive Random-Access Memory Device”, H. Yoshida, K. Sato, US patent US 7, 164, 180 B2

“Circular Polarization Spin Semiconductor Laser Using Magnetic Semiconductor and Laser Beam Generating Method”, H. Yoshida, K. Sato, US patent US 7,254,150 B2

“II-VI group or III-V group compound based single crystal ferromagnetic compound and method for adjusting its ferromagnetic characteristics”, H. Yoshida, K. Sato, Chinese patent No. 02 805828.3

“IV group or III-V group or II-VI group compound based single crystal ferromagnetic compound and method for adjusting its ferromagnetic characteristics”, H. Yoshida and K. Sato, Korean patent No. 10-0703154

“GaN based single crystal ferromagnetic compound and method for adjusting its ferromagnetic characteristics”, H. Yoshida, K. Sato, Japanese patent No.3938284

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Computational nano-materials design for semiconductor spintronics (invited), H. Katayama-Yoshida: International conference on Nanospintronic Design and Realization (ICNDR2007), Dresden, Germany, May 21-25, 2007.

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First-principles design of fabrication process for tera-bit-density nano-magnets in dilute magnetic semiconductors (poster), T. Fukushima: International conference on Nanospintronic Design and Realization (ICNDR2007), Dresden, Germany, May 21-25, 2007.

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Ferromagnetism in Half-Heusler  $\text{Fe}_2\text{A}$  (A=Si, B, C and N) (poster), V. A. Dinh, K. Sato, H. Katayama-Yoshida: 4th International School and Conference on Spintronics and Quantum Information Technology (Spintech-IV), Hawaii, USA, June 17-22, 2007.

Ab initio Design of Self-Organized Tera-Bit Density Nano-Magnets in Dilute Magnetic Semiconductors by Spinodal Decomposition (poster), T. Fukushima, K. Sato, H. Katayama-Yoshida, P. H. Dederichs: 4th International School and Conference on Spintronics and Quantum Information Technology (Spintech-IV), Hawaii, USA, June 17-22, 2007.

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First-Principles SIC-LDA Studies of Magnetism in Transition-Metal-Doped ZnO

(poster), M. Toyoda, H. Akai, K. Sato, H. Katayama-Yoshida: 4th International School and Conference on Spintronics and Quantum Information Technology (Spintech-IV), Hawaii, USA, June 17-22, 2007.

Atom relaxation of H in silicon, K. Shirai, H. Dekura and H. Katayama-Yoshida: 12th International Conference on Phonon Scattering in Condensed Matter, Paris, France, July 15-20, 2007.

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September 10-14, 2007.

New High- $T_c$  Half-Heusler Ferromagnets NiMnZ (poster), V. A. Dinh, K.Sato and H.Katayama-Yoshida: Handai Nanoscience and Nanotechnology International Symposium -Spin, Photonic, and Molecular Devices in Quantum Limit-, Osaka, Japan, September 26-28, 2007.

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Theoretical study of elastic softening of Si with monovacancy (poster), J. Ishisada, K. Shirai, H. Dekura and H. Katayama-Yoshida: Handai Nanoscience and Nanotechnology International Symposium -Spin, Photonic, and Molecular Devices in Quantum Limit-, Osaka, Japan, September 26-28, 2007.

Valence control and metallization of boron by electronic doping (poster), H. Dekura, K.Shirai and H.Katayama-Yoshida: Handai Nanoscience and Nanotechnology International Symposium -Spin, Photonic, and Molecular Devices in Quantum Limit-, Osaka, Japan, September 26-28, 2007.

Control of Impurity Diffusion in Silicon by IR Laser Excitation (poster), K. Shirai, H. Yamaguchi, K. Matsukawa, T. Moriwaki and Y. Ikemoto: 4th International Workshop on Infrared Microscopy and Spectroscopy with Accelerator Based Sources (WIRMS2007), Hyogo, Japan, September 25-29, 2007.

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The effects of monovacancy on the elastic properties of Si (poster), J. Ishisada, K. Shirai and H. Katayama-Yoshida: The 10th Asian Workshop on First-Principles Electronic Structure Calculations, Hiroshima, Japan, October 29-31, 2007.

The theoretical study of impurity doped solid boron (poster), H. Dekura, K. Shirai and H. Katayama-Yoshida: The 10th Asian Workshop on First-Principles Electronic Structure Calculations, Hiroshima, Japan, October 29-31, 2007.

Computational Nano-materials Design for Spin-Currents Control in Semiconductor Nano-spintronics (poster), H. Katayama-Yoshida, T. Fukushima, M. Toyoda, H. Kizaki, V. A. Dinh and K. Sato: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Design of colossal solubility of magnetic impurities for semiconductor spintronics by using the co-doping method (poster), K. Sato and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Spinodal decomposition in  $(\text{In}, \text{Ga})\text{N}$  (poster), M. Eto, M. Toyoda, K. Sato and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Ab-initio Materials Design of CuAlO<sub>2</sub>-based Diluted magnetic Semiconductors (poster), H. Kizaki, K. Sato and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

First Principle Material Design of High-*T<sub>c</sub>* Half-Metallic Half-Heusler Alloys (poster), V. A. Dinh, K. Sato and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Improvement of the getting efficiency of Cu by BO complexes (poster), K. Shirai, K. Matsukawa, H. Yamaguchi, H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

The effects of monovacancy on the elastic properties of Si (poster), J. Ishisada, K. Shirai and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

The stable site and electronic states of Copper in Silicon (poster), H. Yamaguchi, K. Shirai, H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

The theoretical study of elemental solid Boron under high pressure (poster), H. Dekura, K. Shirai and H. Katayama-Yoshida: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Computational Nano-materials Design for Spin-Currents Control in Semiconductor Nano-spintronics (invited), H. Katayama-Yoshida, T. Fukushima, M. Toyoda, H. Kizaki, V. A. Dinh and K. Sato: 3rd Indo-Japan Conference on Ferroics and Multiferroics (under the aegis of DST-JSPS Program), Kolkata, Indo, February 4-6, 2008.

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First-principles Study on the Magnetic Interactions in ZnO-based Dilute Magnetic Semiconductors (poster), M. Toyoda, H. Akai, K. Sato and H. Katayama-Yoshida: APS, American Physical Society March Meeting, New Orleans, USA, March 10-14, 2008.

Design of Colossal Solubility of Magnetic Impurities for Semiconductor Spintronics by the co-doping Method, T. Fukushima, K. Sato and H. Katayama-Yoshida: APS, American Physical Society March Meeting, New Orleans, USA, March 10-14, 2008.

Computational Nano-materials Design for Spin-Currents Control in Semiconductor Nano-Spintronics, H. Katayama-Yoshida, T. Fukushima, V. A. Dinh and K. Sato: APS, AmericanPhysical Society March Meeting, New Orleans, USA, March 10-14, 2008.

First-Principles Study on Electronic Structure of TiO<sub>2</sub> based Dilute Magnetic Semiconductors, H. Kizaki, M. Toyoda, K. Sato and H. Katayama-Yoshida: APS, AmericanPhysical Society March Meeting, New Orleans, USA, March 10-14, 2008.

Design of dilute magnetic semiconductors with room temperature ferromagnetism by controlling spinodal decomposition (invited), K. Sato: APS, AmericanPhysical Society March Meeting, New Orleans, USA, March 10-14, 2008.

Improvement of the gettering efficiency of Cu by BO complexes (poster), K. Shirai, K. Matsukawa, N. Yamaguchi, H. Katayama-Yoshida: The Forum on the Science and Technology of Silicon Materials 2007, Niigata, JAPAN, Nov.12-14, 2007.

Effect of monovacancy on the elastic constant of crystalline silicon (poster), J. Ishisada, K. Shirai, H. Dekura and H. Katayama-Yoshida: The Forum on the Science and Technology of Silicon Materials 2007, Niigata, JAPAN, Nov.12-14, 2007.

The stable site and electronic states of Cu in Si (poster), H. Yamaguchi, K. Shirai and H. Katayama-Yoshida: The Forum on the Science and Technology of Silicon Materials 2007, Niigata, JAPAN, Nov.12-14, 2007.

#### **Contributions to International Conferences and Journals**

|           |                                                                                                         |
|-----------|---------------------------------------------------------------------------------------------------------|
| K. Shirai | 16 <sup>th</sup> International Symposium on Boron, Borides and Related Compounds (Organizing Committee) |
| K. Shirai | The Forum on the Science and Technology of Silicon Materials 2007 (Organizing Committee)                |

#### **Publications in Domestic Meetings**

|                                                                                                                      |           |
|----------------------------------------------------------------------------------------------------------------------|-----------|
| The Physical Society of Japan                                                                                        | 16 papers |
| The Japan Society of Applied Physics                                                                                 | 9 papers  |
| The Magnetism Society of Japan                                                                                       | 1 paper   |
| The 12 <sup>th</sup> symposium on the Physics and Application of Spin-Related Phenomena in Semiconductors (PASPS-12) | 7 papers  |
| Others                                                                                                               | 4 papers  |

#### **Academic Degrees**

##### **Doctor Degree for Science**

|           |                                                                                                                                                                 |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| H. Kizaki | First-Principles Materials Design for Oxide Based Semiconductor Spintronics                                                                                     |
| M. Toyoda | Development and Application of Self-interaction Correction in First-principles Electronic Structure Calculations to Design New Materials for Spintronic Devices |

|              |                                                                                                                                            |
|--------------|--------------------------------------------------------------------------------------------------------------------------------------------|
| T. Fukushima | <i>Ab initio</i> and Statistical Investigations of Electronic Structure and Finite Temperature Magnetism in Dilute Magnetic Semiconductors |
|--------------|--------------------------------------------------------------------------------------------------------------------------------------------|

### Master Degree for Engineering

|           |                                                                                         |
|-----------|-----------------------------------------------------------------------------------------|
| Y. Nakano | Theoretical research of interfacial dipole at benzene/metal, pentacene/metal interfaces |
|-----------|-----------------------------------------------------------------------------------------|

### Master Degree for Science

|              |                                                                                                             |
|--------------|-------------------------------------------------------------------------------------------------------------|
| M. Eto       | <i>Ab initio</i> Design of Nano-structure in $\text{In}_x\text{Ga}_{1-x}\text{N}$ by Spinodal Decomposition |
| H. Yamaguchi | The stable site and electronic states of Cu in Si                                                           |

## Sponsorship

### Grant-in-Aid for Scientific Research on Priority Areas

|         |                                                                           |             |
|---------|---------------------------------------------------------------------------|-------------|
| K. Sato | Development and application of computational nano-materials design engine | ¥10,500,000 |
|---------|---------------------------------------------------------------------------|-------------|

### Grant-in-Aid for Scientific Research for Young Researcher (B)

|         |                                                                                        |            |
|---------|----------------------------------------------------------------------------------------|------------|
| K. Sato | <i>Ab initio</i> calculation for electric transport properties by non-local CPA method | ¥2,000,000 |
|---------|----------------------------------------------------------------------------------------|------------|

### Entrusted Research

|           |                                                                                           |                                                                                                                    |            |
|-----------|-------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|------------|
| K. Shirai | Japan Science and Technology Corporation<br>Research for Promoting Technological Seeds    | Development in Gettering for Transition-Metal Impurities in Semiconductors                                         | ¥2,000,000 |
| K. Shirai | Japan Science and Technology Corporation<br>Collaborative Development of Innovative Seeds | Prediction and Experimental Confirmation of New Gettering Method for Transition-Metal Impurities in Semiconductors | ¥2,400,000 |

### Other Research Fund

|                     |                                          |                                                            |            |
|---------------------|------------------------------------------|------------------------------------------------------------|------------|
| H. Katayama-Yoshida | Japan Science and Technology Corporation | Case study on advanced measurements and analysis           | ¥1,960,000 |
| H. Katayama-Yoshida | Japan Atomic Energy Agency               | Analysis and Materials design simulation in Grid computing |            |

|         |                                                                |                                                                                                                                                                                                                           |            |
|---------|----------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| K. Sato | Kansai Research Foundation for technology promotion (KRF)      | Computational materials design of self-organized nano-structures for semiconductor spintronics                                                                                                                            | ¥1,000,000 |
| K. Sato | Kansai Research Foundation for technology promotion (KRF)      | Support for the participation in ‘International conference on nano-spintronics design and realization’                                                                                                                    | ¥130,000   |
| K. Sato | Inoue Foundation for Science                                   | Support for the participation in ‘4 <sup>th</sup> International school and conference on spintronics and quantum information technology’                                                                                  | ¥150,000   |
| K. Sato | Kansai Research Foundation for technology promotion (KRF)      | Support for the 12 <sup>th</sup> symposium on the Physics and Application of Spin-Related Phenomena in Semiconductors (PASPS-12)                                                                                          | ¥400,000   |
| K. Sato | Research Foundation for the Electrotechnology of Chubu (REFEC) | Support for the 12 <sup>th</sup> symposium on the Physics and Application of Spin-Related Phenomena in Semiconductors (PASPS-12)                                                                                          | ¥250,000   |
| K. Sato | The Murata Science Foundation                                  | Support for the joint research on ‘Ab initio calculation of Curie temperatures of dilute magnetic semiconductors and materials design for semiconductor spintronics’ with Prof. Dederichs from Juelich Research Institute | ¥250,000   |

## Department of Nano-Bio Intelligent Systems Science

Professor: Riichiro MIZOGUCHI  
Assistant Professor: Kouji KOZAKI

### Outlines

The research on development of Nano-Bio intelligent help system, data mining from the nano-bio data, systematization of nano-bio knowledge, ontology engineering is conducted aiming at amalgamation of knowledge research and nano-biotechnology. Special emphasis is placed on systematization of nanotechnology.

It is highly expected that bridging the gap between several domains of nanotechnology to facilitate creative design by enabling reuse of knowledge across these domains. Ontology engineering is an advanced AI technology which has a great potential to achieve the goal. This is why we have been intensively involved in ontology engineering. The concrete objectives include development of nanotechnology ontology, development of function achievement ways for nanomaterials and development of a system for supporting creative design of nanomaterials at the functional level together with an ontology engineering environment.

### Current Research Project

#### Development of Nano-Bio Intelligent Help System based on Ontology Engineering

In the domains including chemical engineering, we develop a common ontology in the light of nanotechnology knowledge systematization. A preliminary ontology has been developed by analyzing textbooks, papers and patents under the consultation of the domain experts. And we developed a prototype of content management system based on the ontology. In 2007, we refined nanotechnology index ontology based on an ontological consideration of function and quality.

We also applied the technology for developing intelligent system based on ontology engineering to the life science domain, and worked out a basic design for advanced database.

#### Development of a System for Supporting Creative Design of Nanomaterials

Aiming at bridging required functions stated by engineers in industries and basic functions(or quality) and at facilitating the creative design, systematization of function achievement ways in a particular domain and development of a support system of functional design of materials are currently conducted in parallel.

In general, a function is achieved by performing multiple sub-functions. The achievement is supported by a physical principle and/or structure of the device or materials which is conceptualized as *Function achievement way*. The decomposition is continued concerning each sub-function to eventually form a function decomposition tree for each device/material. There exist multiple ways of functional decomposition so that the computer can help device/material designers to help their design process by

giving possible alternative ways stored in a function achievement way server.

We have conducted the cross-over collaboration between us and Kawai Labs. The concrete results on this collaboration include development of functional decomposition trees of Nano-film and nano-particle together with a prototype system of creative design support system using a function achievement way server we developed. In addition we described function achievement ways by using Hozo system which we have developed, and we stored them in the server system. And we developed a prototype of the system for supporting creative design of nanomaterials. In 2007, we extended the framework of the system so that it can represent the structure of materials. The system can manage integrated knowledge of functioning-structure-manufacturing process for nano-materials based on ontology engineering, and use the knowledge for supporting creative design of them.

### **An Environment for Ontology Development and its Use**

We developed **Hozo**, an ontology engineering environment, which enables a user to build and use an ontology and instance models. It consists of Ontology editor, Concept factory and ontology server.

#### Ontology editor

It provides a friendly user interface as well as powerful functions necessary for ontology building and editing.

#### Concept factory

A guidance system based on AFM(Activity-First Method) has been implemented to guide ontology developers who build an ontology from technical documents.

#### Ontology server

A server for ontologies and models has been developed. It is based on the client-server architecture and enables human/computer agents to access them through internet.

We published the Ontology editor at the web site (<http://www.hozo.jp>), and we improved the Graphical User Interface of the system based on feedbacks from its users. And we developed API for ontology-based system and applied it to our content management system and creative design support system.

In 2007, we improved Hozo for construction of a medical ontology. Its new functions include an extension of OWL support, a function to import semi-structured data, multiple label management and so on.

## **Publications**

### **Original Papers**

The Model of Roles within Ontology Development Tool:Hozo, R. Mizoguchi, E. Sunagawa, K. Kozaki and Y. Kitamura: J. of Applied Ontology, 2 (2) (2007) 159-179.

Development of a Design Supporting System for Nano-Materials based on a Framework



for Integrated Knowledge of Functioning-Manufacturing Process, S. Tarumi, K. Kozaki, Y. Kitamura, H. Tanaka and R. Mizoguchi: Transactions of the Japanese Soc. for Artificial Intelligence, 23 (1) (2008) 36-49.

### **International Conferences**

Development of a Design Supporting System for Nano-Materials based on a Framework for Integrated Knowledge of Functioning-Manufacturing Process, \*S. Tarumi, K. Kozaki, Y. Kitamura, H. Tanaka and R. Mizoguchi: The 10th IASTED International Conference Intelligent Systems and Control(ISC2007),Cambridge, Massachusetts, USA, Novemb 19-21, 2007.

A Framework for Cooperative Ontology Construction Based on Dependency Management of Modu, \*K. Kozaki, E. Sunagawa, Y. Kitamura and R. Mizoguchi: International Workshop on Emergent Semantics and Ontology Evolution (ESOE2007), Busan, Korea, November 12, 2007.

Role Representation Model Using OWL and SWRL, \*K. Kozaki, E. Sunagawa, Y. Kitamura and R. Mizoguchi: 2nd Workshop on Roles and Relationships in Object Oriented Programming, Multiagent Systems, and Ontologies, Berlin, July 30-31, 2007.

Distributed and Collaborative Construction of Ontologies Using Hozo, \*K. Kozaki, E. Sunagawa, Y. Kitamura and R. Mizoguchi: Workshop on Social and Collaborative Construction of Structured Knowledge, Banff, Canada, May 8, 2007.

### **Contributions to International Conferences and Journals**

|             |                                                                                                                                                                                                          |
|-------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| R.Mizoguchi | Semantic Web Science Association (Vice-president)                                                                                                                                                        |
| R.Mizoguchi | International Artificial Intelligence in Education Society (Executive Committee)                                                                                                                         |
| R.Mizoguchi | Asia-Pacific Society for Computers in Education(APSCE) (Board member)                                                                                                                                    |
| R.Mizoguchi | The 15th International Conference on Computers in Education (ICCE2007) (PC member)                                                                                                                       |
| R.Mizoguchi | The 12 <sup>th</sup> Conference of the Spanish Association for Artificial Intelligence and The Workshop on Artificial Intelligence Technology Transfer (CAEPIA - TTIA '07) (Scientific Committee member) |
| R.Mizoguchi | The 2nd European Conference on Technology Enhanced Learning (EC-TEL 2007) (PC member)                                                                                                                    |
| R.Mizoguchi | The 13 <sup>th</sup> International Conference on Artificial Intelligence in Education (AIED2007) (PC member)                                                                                             |
| R.Mizoguchi | The 4 <sup>th</sup> European Semantic Web Conference (ESWC2007) (PC member)                                                                                                                              |
| R.Mizoguchi | The 7th IEEE International Conference on Advanced Learning Technologies (ICALT'07) (PC member)                                                                                                           |
| R.Mizoguchi | The 2007 IEEE International Conference on Information Reuse                                                                                                                                              |

|             |                                                                                                                            |  |
|-------------|----------------------------------------------------------------------------------------------------------------------------|--|
|             | and Integration (IEEE IRI-07) (PC member)                                                                                  |  |
| R.Mizoguchi | The 16th International World Wide Web Conference Semantic Web Track (PC Chair)                                             |  |
| R.Mizoguchi | The 4th International Conference on Knowledge Capture (K-CAP 2007) (PC member)                                             |  |
| R.Mizoguchi | The 6th international semantic web conference (ISWC2007) (General Chair)                                                   |  |
| R.Mizoguchi | The 5th International Workshop on Applications of Semantic Web Technologies for E-Learning (SWEL'07) (Workshop Organizers) |  |
| R.Mizoguchi | Workshop on Semantic Technology for Learning (PC member)                                                                   |  |
| R.Mizoguchi | International Journal of Advanced Engineering Informatics (Editorial board)                                                |  |
| R.Mizoguchi | International Journal of Applied Ontology (Editorial board)                                                                |  |
| R.Mizoguchi | Research and Practice in Technology Enhanced Learning (Editorial board)                                                    |  |
| R.Mizoguchi | International Journal of Artificial Intelligence in Education (Editorial board)                                            |  |
| R.Mizoguchi | Frontiers in AI and Application (Editorial board)                                                                          |  |
| R.Mizoguchi | International Journal of Web Engineering and Technology (Editorial board)                                                  |  |
| R.Mizoguchi | International Journal of Web Semantics (Editorial board)                                                                   |  |
| R.Mizoguchi | Journal of Educational Technology & Society (Editorial board)                                                              |  |
| R.Mizoguchi | The 2 <sup>nd</sup> Asian Semantic Web Conference (Steering committee member)                                              |  |
| K.Kozaki    | The 6th international semantic web conference (ISWC2007) (PC member)                                                       |  |

#### Publications in Domestic Meetings

|                                                                       |          |
|-----------------------------------------------------------------------|----------|
| Japanese Society for Artificial Intelligence                          | 4 papers |
| The institute of Electronics, information and communication engineers | 1 papers |

### Sponsorship

#### Grant-in-Aid for Scientific Research on Priority Areas

|              |                                                               |            |
|--------------|---------------------------------------------------------------|------------|
| R. Mizoguchi | Technical documents integration based on an artifact ontology | ¥5,200,000 |
|--------------|---------------------------------------------------------------|------------|

#### Grant-in-Aid for Young Scientists (B)

|           |                                                                                                           |          |
|-----------|-----------------------------------------------------------------------------------------------------------|----------|
| K. Kozaki | A Development of Knowledge Management System Based on Ontology and its Application for Nanotech Knowledge | ¥900,000 |
|-----------|-----------------------------------------------------------------------------------------------------------|----------|

### Entrusted Research

|              |                         |                                                                                                                                |             |
|--------------|-------------------------|--------------------------------------------------------------------------------------------------------------------------------|-------------|
| R. Mizoguchi | The University of Tokyo | Research on development of a medical knowledge database for medical information systems; Design of a semantic relational model | ¥10,000,000 |
|--------------|-------------------------|--------------------------------------------------------------------------------------------------------------------------------|-------------|

**Cooperative Research**

|              |                    |       |                                                          |            |
|--------------|--------------------|-------|----------------------------------------------------------|------------|
| R. Mizoguchi | Idemitsu Co., Ltd. | Kosan | Development of knowledge base systems for nano-materials | ¥3,300,000 |
|--------------|--------------------|-------|----------------------------------------------------------|------------|

## Department of Nanotechnology Transfer

Guest Professor      Anishchik Sergey VLADIMIRIVICH (2006.8.21~2007.8.20 )

### Outlines

On the next generation nano-fabrication, for further refining, the Extreme Ultra Violet (EUV) light with the wavelength of 13.5 nm will be used. However, for the EUV lithography, there are many problems remain to be solved, because the photon energy exceeds the ionization potential of materials. In order to solve these problems and actualizes the next generation extremity nano-fabrication, the study of ultrafast phenomena in reaction process is necessary. The reactions of ionization, excitation geminate pair recombination, and so on should be understood. In the department, the geminate pair recombination process in the none-polar solvent was studied theoretically and experimentally.

### Achievement

In our research, the geminate ion recombination was studied by using the picosecond pulse radiolysis at the wavelength of 523 nm. At this wavelength, not only the kinetics of the cation radical are observed, but also the formation of excited states due to the geminate ion recombination and the decay of the excited states can be studied, because of the overlap of the cation radical and the excited state absorbance. In our experiments, the kinetics of the cation radical in n-dodecane and n-hexane were observed and studied with/without the electron scavengers. The experimental dynamics were compared with the theoretical simulation based on the Smoluchowski equation. It is found that the experimental data are in good agreement with the theoretical description at  $> 50$  ps. The ratio of the yields of the excited states formed by the direct excitation/energy transfer was estimated to be 10% in n-dodecane, and 17% in n-hexane.

## Department of Nanotechnology Transfer

Guest Associate Professor: Adhikari SOUMYAKANTI (2007.9.3~2007.12.3)

### Outlines

Lithography technology used for semiconductor mass production has been arrived at the level processing less than 100 nm size. Extreme ultraviolet and electron beam are regarded as promising exposure sources to achieve a higher resolution. However in order to realize that, a lot of subjects about the ionizing radiation responsiveness to materials remain unclear. The elucidation of the phenomenon caused by ionizing radiation is not only interesting chemically and physically but also is expected for a development of future top-down nanotechnology.

### Achievement

#### Pulse radiolysis of *p*-dioxane

*p*-Dioxane is cyclic ether, however deprotonation efficiency of the radical cation produced by an exposure to radiation is low, and the different radiation chemical reaction from that in tetrahydrofuran with high deprotonation efficiency is expected. Radiation chemical reactions were studied by means of pulse radiolysis and the dynamics of related intermediates were made clear.

## Department of Nanotechnology Transfer

Guest Professor: Chan IM (2006.12.10-2007.3.10)

### Outlines

$\pi$ -conjugated Polymer is considered to be efficient organic LED materials. It is important to elucidate mechanism of OLED, based on the excitation energy transfer, and energy quenching of  $\pi$ -electron chromophore in single polymer chain for the development of LED materials.

### Achievement

The following two original research manuscripts were submitted for publication in scientific journals.

- 1) Triplet Level Dependent Photoluminescence and Photoconduction Properties of  $\pi$ -Conjugated Polymer Thin Films Doped by Iridium Complexes.
- 2) Comparing Electroluminescence Efficiency and Photoluminescence Quantum Yield of Fluorene-based  $\pi$ -Conjugated Copolymers with Narrow Band-gap Comonomers.

# Division of Nanocharacterization

## Outlines

Division of Nanocharacterization has four departments: Department of Advanced Nanostructural Characterization, Department of Advanced Characterization for Nano-Processing, Department of Quantum Materials and Devices Characterization, and Department of Computational Nanocharacterization. This division aims at development and establishment of high-precision methods in evaluating nanoproceses, nanostructures and quantum-materials/devices specially suited for the unique features of nanotechnology, focusing on atomic-level surface layer formation, atomic arrangements and their relations to electron states, next-generation materials/devices properties.

## Achievements

- Local structure analysis of Fe-Si metastable phases using nanobeam electron diffraction
- Structure analysis of phase change recording materials in real devices
- Elucidation of fundamental mechanism of tip-induced lithography of semiconductor surfaces studied by low-energy electron-beam irradiation.
- Finding of Plasmon-induced structural instability on Si surfaces
- Study on the initial process of Graphite-to-Diamond phase transition induced by femtosecond laser excitation.
- Control of nanostructures formed by preferential bond rupture of non-metallic atoms on III-V semiconductor surfaces by means of tip-induced local hole injection.
- Nano-characterization of GaN-based magnetic semiconductor nanorod structures.
- XAFS characterization of atomic arrangement of (In,Ga,Cr)N new diluted magnetic semiconductors.
- Nano-characterization of Fe/GaN hybrid structures.

## Department of Advanced Nanostructural Characterization

Professor: Yoshihiko HIROTSU  
Research Associate: Muneyuki NAITO

### Outlines

The purpose of this department is to develop new electron microscopy methods to characterize atomic structures, atomic bonding and electronic structures of functional nanomaterials in order to contribute to the development and realization of novel functional materials and devices.

### Current Research Project

#### Local structure analysis of Fe-Si metastable phases

Thermal annealing-induced recrystallisation in Fe ion-implanted Si was investigated by transmission electron microscopy. Single crystals of Si(111) were implanted with 120 keV Fe ions to a fluence of  $1.0 \times 10^{17}/\text{cm}^2$  at cryogenic temperature. A buried amorphous Fe-Si layer in an amorphous Si matrix was formed in the as-implanted sample. Nanobeam electron diffraction revealed that metastable  $\alpha\text{-FeSi}_2$  precipitates embedded in the amorphous Si matrix were formed after annealing at 350°C for 8 h. The formation of this  $\alpha\text{-FeSi}_2$ -derived phase is unusual, because it has been observed only in epitaxially grown thin films. The metastable  $\alpha\text{-FeSi}_2$  consists of three types of domains whose *c*-axes are oriented 90° angles relative to one another. We suggested that a phase transformation from  $\text{Fe}_{1-x}\text{Si}$  with CsCl structure to the metastable  $\alpha\text{-FeSi}_2$  took place during annealing. This proposition is supported by structural similarities between these two phases.

#### Structure analysis of phase change recording materials in real devices

We have investigated the structure of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  recording materials in real phase-change optical disks by transmission electron microscopy in combination with high resolution electron microscopy and nano-beam electron diffraction. The as-deposited  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin films in the optical disk possessed an amorphous structure and were crystallized to a metastable phase with NaCl structure by laser annealing. The recording marks formed in the disk were directly observed by cross-sectional TEM. It was found that the amorphous phase having the structure similar to the as-deposited film was reproduced in the recording marks.

### Publications

#### Original Papers

Direct Imaging of Local Atomic Ordering in a Pd-Ni-P Bulk Metallic Glass using Cs-Corrected Transmission Electron Microscopy, A. Hirata, Y. Hirotsu, T. G. Nieh, T. Ohkubo, N. Tanaka: Ultramicroscopy, 107 (2007) 116-123.

Local Atomic Structure Analysis of Zr-Ni and Zr-Cu Metallic Glasses using Electron



Diffraction, A. Hirata, T. Morino, Y. Hirotsu, K. Itoh, T. Fukunaga: Mater. Trans., 48 (2007) 1229-1303.

Voronoi Analysis of the Structure of Ni-Zr-Al Ternary Metallic Glass, T. Fukunaga, K. Itoh, T. Otomo, K. Mori, M. Sugiyama, H. Kato, M. Hasegawa, A. Hirata, Y. Hirotsu, A. C. Hannon: Mater. Trans., 48 (2007) 1698-1702.

Structural Analysis of BiFeO<sub>3</sub> Polycrystalline Films by Transmission Electron Microscopy, H. Naganuma, A. Kovács, A. Hirata, Y. Hirotsu, S. Okamura: Mater. Trans., 48 (2007) 2370-2377.

Fabrication of L10-PdCoFe Nanocrystalline Particles with Tilted Magnetic Easy Axis, A. Kovács, Y. Hirotsu: Appl. Phys. Lett., 91 (2007) 193106(1)- 193106(3).

Melt-Spun L10 Fe-Pt-(Zr, Nb and Ti)-B Nanocrystalline Alloys with High Coercivity, A. Makino, T. Bitoh, A. Inoue, Y. Hirotsu: Mater. Sci. Eng. A, 449-451 (2007) 66-70.

Magnetic Properties and Structure of Fe-Pt-M-B (M=Zr, Nb and Ti) Alloys Produced by Quenching Technique, A. Makino, T. Bitoh, A. Inoue, Y. Hirotsu: J. Alloys Comp., 434-435 (2007) 614-617.

Magnetic Properties and Microstructure of FePt-M-B (M=Zr, Nb, La) Films, H. Okumura, S. Nishinakagawa, T. Bitoh, A. Makino, K. Sato, Y. Hirotsu: J. Magn. Magn. Mater., 310 (2007) 2527-2528.

Particle Size Dependence of Atomic Ordering and Magnetic Properties of L10-FePd Nanoparticles, H. Naganuma, K. Sato, Y. Hirotsu: J. Magn. Magn. Mater., 310 (2007) 2356-2358.

Strong Perpendicular Magnetic Anisotropy of Fe-Pd Nanocrystalline Particles Enhanced by Co Addition, A. Kovács, K. Sato, Y. Hirotsu: J. Appl. Phys., 101 (2007) 033910(1)-033910(4).

Low-Temperature Atomic Ordering of Oriented L10-FePtCu Nanoparticles with High Areal-Density Characterized by Transmission Electron Microscopy and Electron Diffraction, H. W. Ryu, K. Sato, Y. Hirotsu: Mater. Trans., 48 (2007) 903-908.

High-Resolution Transmission Electron Microscopy Analysis of L10 Ordering Process in Fe/Pd Thin Layers, A. Kovács, K. Sato, Y. Hirotsu: J. Appl. Phys., 102 (2007) 123512(1)-123512(4).

Improvement of Structural and Magnetic Properties of L10-FePd Nanocrystals by Co Addition, A. Kovács, K. Sato, Y. Hirotsu: IEEE Trans. Mag., 43 (2007) 3097-3099.

Synthesis of Iron Silicides by Electron-Beam Evaporation: Effects of Substrate Pre-Baking Temperature and Fe Deposition Thickness, J. H. Won, K. Sato, M. Ishimaru, Y. Hirotsu: Jpn. J. Appl. Phys., 46 (2007) 732-737.

Effect of Ionization Rates on Dynamic Recovery Processes during Electron-Beam Irradiation of 6H-SiC, I.-T. Bae, W. J. Weber, M. Ishimaru, Y. Hirotsu: Appl. Phys. Lett., 90 (2007) 121910(1)-121910(3).

Exchange Interactions in Hydrogen-Induced Amorphous YFe<sub>2</sub> (invited), K. Suzuki, K. Ishikawa, K. Aoki, J. M. Cadogan, M. Ishimaru, Y. Hirotsu: J. Non-Cryst. Solids, 353 (2007) 748-752.

Post-Annealing Recrystallization and Damage Recovery Process in Fe Ion Implanted Si, M. Naito, A. Hirata, M. Ishimaru, Y. Hirotsu: Nucl. Instrum. Meth. B, 257 (2007) 340-343.

Ion-beam-induced phase transformations in d-Sc<sub>4</sub>Zr<sub>3</sub>O<sub>12</sub>, M. Ishimaru, Y. Hirotsu, M. Tang, J. A. Valdez, K. E. Sickafus: J. Appl. Phys., 102 (2007) 063532(1)-063532(7).

Formation process of sharp-pointed structures on GaN nanorods during RF-MBE growth and their field emission characteristics, M. Terayama, S. Hasegawa, K. Uchida, M. Ishimaru, Y. Hirotsu, H. Asahi: Physica Status Solidi C, 4 (2007) 2371-2374.

Formation processes of iron silicide nanoparticles studied by ex situ and in situ transmission electron microscopy, J. H. Won, A. Kovács, M. Naito, M. Ishimaru, Y. Hirotsu: J. Appl. Phys., 102 (2007) 103512(1)-103512(7).

Change of Nanostructure in (Fe<sub>0.5</sub>Co<sub>0.5</sub>)<sub>72</sub>B<sub>20</sub>Si<sub>4</sub>Nb<sub>4</sub> Metallic Glass on Annealing, A. Hirata, Y. Hirotsu, K. Amiya, N. Nishiyama, A. Inoue: Mater. Sci. Forum, 539-543 (2007) 2077-2081.

Low-Temperature Synthesis of Oriented L10-FePtCu Nanoparticles with High Coercivity, H. W. Ryu, K. Sato, Y. Hirotsu: Solid State Phenom., 124-126 (2007) 855-858.

Structure and Magnetic Properties of Nanocrystalline Pd-Co and Pd-Co-Fe Layers, A. Kovács, K. Sato, Y. Hirotsu: Solid State Phenom., 124-126 (2007) 907-910.

Direct Synthesis of Isolated L10-FePtCu Nanoparticles by RF-Magnetron Sputtering, H. W. Ryu, K. Sato, Y. Hirotsu: Solid State Phenom., 127 (2007) 129-134.

### **Review Papers**

Advanced Electron Beam Techniques, Y. Hirotsu and Y. Yoshida, Hamon 17 (2007) 75-80 (in Japanese).

Local Structure and Crystallization Process of Amorphous Fe-Si Thin Layers, M. Naito, A. Hirata, M. Ishimaru, and Y. Hirotsu, J. Cryst. Soc. Jpn. 49 (2007) 115-121 (in Japanese).

Electron Diffraction Structure Analysis of Phase-Change Recording Materials, M. Naito, M. Ishimaru, and Y. Hirotsu, Materia Japan 46 (2007) 652-659 (in Japanese).

### **International Conferences**

Medium Range Order Structures and their Changes in the Course of Primary Crystallization in some Metallic Glasses (invited), \*Y. Hirotsu: WPI & IFCAM Joint Workshop, Sendai, Japan, February 18-19, 2007.

Fabrication of Oriented Hard-Magnetic Alloy Nanoparticles and Their Characterization (invited), \*Y. Hirotsu, K. Sato, A. Kovacs, H.Naganuma, H.W. Ryu: 1st International Symposium on Advanced Magnetic Materials, Jeju, Korea, May 28-June 1, 2007.

Observation of Local Structural Change in the Course of Primary Crystallization of Metallic Glasses (invited), \*Y. Hirotsu, A. Hirata: 14th International Symposium on Metastable and Nano Materials, Corfu, Greece, August 26-30, 2007.

Local Structure Studies of Metallic Glasses using HREM and Electron Diffraction (invited), \*Y. Hirotsu, A. Hirata: Workshop on Fundamental Issues in Metallic Glasses, Guilin and Kunming, China, October 22-26, 2007.

### **Contributions to International Conferences and Journals**

Y. Hirotsu                      7th Japan-Polish Joint Seminar on Materials Analysis  
(Organizing Committee)

### **Publications in Domestic Meetings**

|                                               |          |
|-----------------------------------------------|----------|
| The Japan Society of Applied Physics          | 2 papers |
| Japanese Society of Microscopy                | 1 paper  |
| The Japan Institute of Metals                 | 1 paper  |
| Japan Society of Powder and Powder Metallurgy | 1 paper  |

### **Sponsorship**

#### **Grant-in-Aid for Scientific Research on Priority Areas**

|            |                                                                                   |            |
|------------|-----------------------------------------------------------------------------------|------------|
| Y. Hirotsu | In situ observation of atomistic structures in metallic liquid and metallic glass | ¥9,800,000 |
|------------|-----------------------------------------------------------------------------------|------------|

#### **Grant-in-Aid for Scientific Research (S)(2)**

|            |                                                                                                   |             |
|------------|---------------------------------------------------------------------------------------------------|-------------|
| Y. Hirotsu | Fabrication and characterization of hard magnetic alloy nanoparticles produced by vapor quenching | ¥14,430,000 |
|------------|---------------------------------------------------------------------------------------------------|-------------|

### **Entrusted Research**

|            |                                                                               |                                                                                      |            |
|------------|-------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|------------|
| Y. Hirotsu | NEDO<br>(Advanced Materials Technology Utilizing Glassy Metals for Commercial | Nano-structure Analysis for the Evaluation of Mechanical Properties in Glassy Metals | ¥3,150,000 |
|------------|-------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|------------|

|            |                                                |                                                                                          |          |
|------------|------------------------------------------------|------------------------------------------------------------------------------------------|----------|
| Y. Hirotsu | Uses)<br>Matsushita<br>Electric Works,<br>Ltd. | Structure Characterizatiuon of<br>Inorganic and Organic<br>Materials on Glass Substrates | ¥400,000 |
|------------|------------------------------------------------|------------------------------------------------------------------------------------------|----------|

## Department of Advanced Characterization for Nano-Processing

Professor: Katsumi TANIMURA  
Associate Professor: Jun'ichi KANASAKI

### Outlines

For fabricating highly functional nano-structured devices in future technology, it is important to establish the ways to control structures and compositions of materials in atomic levels. Electronic excitations, which induce and promote atomic processes with strongly site-sensitive rates, can be a promising method for creating nano-scaled structures possessing new properties and functions, that are not achieved by conventional thermal process. Our targets are to understand completely the fundamentals of underlying physics concerning the excitation-induced atomic processes, and finally to establish advanced surface nano-processing technologies fully exploiting unique features of electronic-excitation effects. For this purpose, we have studied laser or low-energy electron induced structural changes of semiconductor and graphite surfaces by means of the direct imaging of the surface structures using scanning tunneling microscopy (STM).

### Current Research Project

#### • Structural Changes of Si Surfaces Induced by Low Energy Electron Beams with High-Energy Resolution

The quantum nature of low-energy (several eV - 10eV) electrons (LEEs) is obvious in most processes, and the Born approximation cannot be used for describing the scattering of LEEs. Therefore, the primary mechanisms of the LEE interaction with solids have not yet been completely understood. We study the structural responses of semiconductor surfaces induced by LEE beams with high energy resolution (0.3eV), in order to establish an advanced surface nano-processing technology fully exploiting the excitation-induced structural changes. Obtained results are as follows:

- 1) We have studied physical mechanisms of the LEE-beam induced bond breaking on the Si(001)-2x1:H surface, though the surface has been one of model systems for the tip-induced surface reactions. We have demonstrated that the LEE-beam induced bond rupture is due to inelastic electronic excitation of bonding-to-antibonding states of Si-H bond.
- 2) On Si(111)7x7surface, LEEs with energies higher than 7.5 eV induce the bond rupture at adatom sites on the topmost layer of the reconstructed surface.
- 3) The bond rupture efficiency has been measured as a function of the energy  $E_{av}$ , the maximum energy available for inelastic excitation. The efficiency shows the maximum at  $E_{av}=12\text{eV}$ , and decreases rapidly when the energy moves away from the energy.
- 4) The morphological features of LEE-induced vacancies at adatom sites are the same as those for the laser-excitation.

The available energy giving the maximum efficiency coincides with the plasma excitation energy of Si crystal. The obtained results provide the first evidence for the bond rupture on semiconductor surfaces induced by plasmon excitation. In the future, further investigations will clarify some crucial factors that govern surface bond rupture induced by LEE excitation of semiconductor surfaces.

#### • **Structural Instability of Graphite Surface by Femtosecond-Laser Excitation**

We have obtained the first direct atomic-scale evidence of the non-thermodynamic formation of  $sp^3$ -type interlayer bonds under valence excitation with fs-laser pulses.

##### **1. Formation of Nanometer-Scaled Structures on the Graphite Surface by Femtosecond-Laser Excitation**

Direct imaging of the excited surfaces by means of STM has shown two types of nanometer-scaled structures, which are accompanied with lateral displacement of surface atoms along one of  $\langle 1-100 \rangle$  directions from their original sites. The scanning tunneling spectroscopic measurement has revealed an increase of the density of unoccupied states around 0.3 eV relative to the Fermi level at the nano-structures, suggesting the formation of a pseudo energy gap. Taking into account theoretical predictions, the observed features of the nano-structures are indicative of the formation of  $sp^3$ -type bonds between neighboring layers.

##### **2. Fragmentary Removal of Double Graphene Layers by Femtosecond-Laser Excitation**

We observed circular craters on the surface excited by femtosecond laser pulses of intensities just below the threshold for ablation. The craters were typically several nm in diameter, where about  $10^2$  surface atomic sites were included, and the exposed region inside the crater was flat on an atomic scale. The height profiles measured across the rim of craters indicate the depth of craters is about twice as high as that for a surface step of single atomic height, demonstrating the flakes of double graphene layers are emitted in cluster. The removal of double graphene layers, a novel mode of laser-ablation observed first by the present study, indicates clearly the formation of strong interlayer  $sp^3$ -type bonds between the two graphene layers.

### **Publications**

#### **Original Papers**

Fermi-Level Dependent Morphology in Photoinduced Bond Breaking on (110) Surfaces of III-V Semiconductors, J. Kanasaki, E. Inami, and K. Tanimura, Surface Science 601 [11] (2007) 2367-2372.

Electronic Bond Rupture of Si atoms on Si(111)-(2x1) Induced by Valence Excitation, E. Inami and K. Tanimura, Physical Review B 76 [3] (2007) 035311-1-11.

#### **International Conferences**

Hydrogen Removal from Si(001)-2x1:H Surface Induced by Low-Energy Electron

Beam Excitation, K. Ichihashi, \*J. Kanasaki, and K. Tanimura, Handai Nanoscience and Nanotechnology International Symposium 2007, Osaka, Japan, September 26-28, 2007

Scanning Tunneling Microscopy Study on Hydrogen Removal from Si(001)-(2x1):H Surface Excited with Low-Energy Electron Beams, J. Kanasaki, K. Ichihashi, K. Tanimura, 11<sup>th</sup> SANKEN International Symposium、6<sup>th</sup> Nanotechnology Center International Symposium, 1<sup>st</sup> MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Photo-induced Structural Changes on Si(111)-(2x1), E. Inami, J. Kanasaki, K. Tanimura, 11<sup>th</sup> SANKEN International Symposium、6<sup>th</sup> Nanotechnology Center International Symposium, 1<sup>st</sup> MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

### **Contributions to International Conferences and Journals**

K.Tanimura                      International Workshop on Desorption Induced by Electronic Transitions (International Steering Committee)

### **Publications in Domestic Meetings**

|                               |          |
|-------------------------------|----------|
| The Physical Society of Japan | 2 papers |
| Others                        | 4 papers |

### **Sponsorship**

#### **Grant-in-Aid for Specially Promoted Science**

|             |                                                     |               |
|-------------|-----------------------------------------------------|---------------|
| K. Tanimura | Dynamical Studies of Photoinduced Phase Transitions | ¥ 188,110,000 |
|-------------|-----------------------------------------------------|---------------|

#### **Grant-in-Aid for Scientific Research (A)**

|             |                                                                                      |             |
|-------------|--------------------------------------------------------------------------------------|-------------|
| K. Tanimura | Dynamical properties of excited semiconductor surfaces with two-dimensional features | ¥ 2,300,000 |
|-------------|--------------------------------------------------------------------------------------|-------------|

#### **Grant-in-Aid for Exploratory Research**

|             |                                                                                         |             |
|-------------|-----------------------------------------------------------------------------------------|-------------|
| K. Tanimura | Graphite-to-Diamond Structural Phase Transformation Induced by Visible-Light Excitation | ¥ 1,500,000 |
|-------------|-----------------------------------------------------------------------------------------|-------------|

#### **Grant-in-Aid for Scientific Research (C)**

|             |                                                                                                 |          |
|-------------|-------------------------------------------------------------------------------------------------|----------|
| J. Kanasaki | Structural Instability of Semiconductor Surfaces Induced by Low-Energy Electron Beam Excitation | ¥650,000 |
|-------------|-------------------------------------------------------------------------------------------------|----------|

#### **Other Research Fund**

|             |                                           |                                                                                 |            |
|-------------|-------------------------------------------|---------------------------------------------------------------------------------|------------|
| J. Kanasaki | Iketani Science and Technology Foundation | Control of Nano-Scaled Structures on Semiconductor Surfaces by Photo-Excitation | ¥1,500,000 |
|-------------|-------------------------------------------|---------------------------------------------------------------------------------|------------|

# Department of Quantum Materials and Devices Characterization

Professor: Hajime ASAHI  
Assistant Professor: Yi-Kai ZHOU

## Outlines

The department of quantum materials and devices characterization makes researches on new characterization methods and the characterization of structural and physical properties of quantum materials and quantum devices in order to contribute to the development and realization of novel functional quantum materials and devices.

- Development and application of nano-characterization methods for the physical properties of quantum materials.
- Development and application of nano-characterization methods for the structural and physical properties of quantum devices including next generation LSIs.
- Development and application of nano-characterization methods for the device properties of quantum devices.

## Current Research Project

### 1. Nano-Characterization of GaN-Based Magnetic Semiconductor Nanorod Structures

Quantum nanostructures are basic structures for devices. Nanostructures using diluted magnetic semiconductors perform very important roles for the fabrication of spin devices. We doped Cr into GaN nanorods and formed GaCrN nanorods using molecular beam epitaxy (MBE) method. Nano-characterization offered very important information about how to grow the GaCrN nanorods. We firstly clarified the relation between GaN nanorods and their growth conditions. Scanning electron microscopy (SEM) observation revealed that the GaN rods are self-formed by the growth of GaN at high temperatures on the low temperature-grown GaN buffer layer because of the formation of nucleation sites. The surface structure, the cross-sectional structure and the concentration of the GaCrN nanorods were also evaluated by atomic force microscopy (AFM), transmission electrons microscopy (TEM) and electron energy-loss spectroscopy (EELS), respectively. The results show that the GaCrN nanorods contain the Cr concentration below 1%, and Cr atoms tend to segregate at the periphery of the nanorods. When the growth temperature was decreased to 550°C, it was found that Cr concentration of 2~3% were uniformly incorporated into GaCrN nanorods.

### 2. Nano-Characterization of Fe/GaN Hybrid Structures

Spin injection behavior from magnetic metals into diluted magnetic semiconductors (DMSs) is very important to realize semiconductor spintronics devices. Fe metals were grown on GaN and their crystal structures, growth mode and magnetic properties were intensively studied this year. It was found that magnetic characteristics greatly depend on the amount of deposited Fe metals and their structures.

### 3. XAFS Characterization of atomic arrangement of (In,Ga,Cr)N new diluted



## **magnetic semiconductors**

New diluted magnetic semiconductor (In,Cr,Ga)N is a candidate material to fabricate circular polarization spin semiconductor laser diodes, which are useful for quantum cryptography based on optical communication. InCrN and a new quaternary alloy (In,Ga,Cr)N were synthesized by MBE at growth temperature of 350°C. Their structural properties were studied with X-ray diffraction and X-ray absorption fine structure (XAFS). It was found that low temperature growth enables the growth of InCrN and (In,Ga,Cr)N with higher Cr contents, while they were not crystallized at higher substrate temperature (450°C). XAFS studies suggest that Cr atoms substitute on cation sites and no trace of locally formed secondary phases, such as Cr cluster, CrN (NaCl type) and Cr<sub>2</sub>N, in the grown InCrN and (In,Ga,Cr)N layers.

## **Publications**

### **Original Papers**

Cr atom alignment in Cr-delta-doped GaN, S. Kimura, S. Emura, H. Ofuchi, Y. Nakata, Y.K. Zhou, C.W. Choi, Y. Yamauchi, S. Hasegawa and H. Asahi: American Institute of Physics, CP 882 (2007) 410-412.

Growth and Characterization of Ferromagnetic Cubic GaCrN: Structural and magnetic properties, S. Kimura, S. Emura, H. Ofuchi, Y. Zhou, S. Hasegawa and H. Asahi: J. Cryst. Growth, 301-302 (2007) 651-655.

Formation process of sharp-pointed structures on GaN nanorods during RF-MBE growth and their field emission characteristics, M. Terayama, S. Hasegawa, K. Uchida, M. Ishimaru, Y. Hirotsu and H. Asahi: Phys. Stat. Sol. (c), 4 (7) (2007) 2371-2374.

Molecular-beam epitaxy growth and characterization of ferromagnetic cubic GaCrN on GaAs substrate, S. Kobayashi, S. Shanthi, S. Kimura, Y.K. Zhou, S. Emura, S. Hasegawa and H. Asahi: J. Cryst. Growth, 308 (1) (2007) 58-62.

High Gd concentration GaGdN grown at low temperatures, Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi: Journal of Superconductivity and Novel Magnetism, 20 (6) (2007) 429-432.

### **Review Papers**

Semiconductor Nanospintronics and Devices, Y.K. Zhou and H. Asahi, Vacuum 49(12) (2006) 722-727 (in Japanese).

## **Patents**

### **International Conferences**

MBE Growth and Characterization of Rare-Earth Doped Nitride Semiconductors for Spintronics (INVITED) (invited), H. Asahi, Y.K. Zhou, S. Emura and S. Hasegawa: E-MRS2007.

High Gd concentration GaGdN grown at low temperature (poster), Y.K. Zhou, S.W.

Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi: SpinTech-IV.

Enhancement of magnetic moment in GaGdN/GaN superlattice structure (poster), Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi: ChinaNANO 2007.

Enhancement of magnetic moment in GaGdN/GaN superlattice structure, Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi: Material Today Asia.

Growth and characterization of InCrN and (In,Ga,Cr)N diluted magnetic semiconductors (poster), S. Kimura, S. Emura, Y. Hiromura, Y.K. Zhou, S. Hasegawa and H. Asahi: 7th International Conference on Nitride Semiconductors.

Deformation of CrN<sub>4</sub> tetrahedron site symmetry in GaCrN detected by X-ray linear dichroism (poster), S. Emura, S. Kimura, H. Tambo, Y. Hiromura, Y.K. Zhou, S. Hasegawa and H. Asahi: 11th SANKEN International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium.

Enhancement of magnetic properties in GaGdN/GaN superlattice structure and low-temperature-grown GaGdN layer (poster), Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi: 11th SANKEN International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium.

#### **Contributions to International Conferences and Journals**

|          |                                                                                                                 |
|----------|-----------------------------------------------------------------------------------------------------------------|
| H. Asahi | 2007 International Conference on Solid State Devices and Materials (Program Committee member)                   |
| H. Asahi | International Symposium on Compound Semiconductors 2007 (Organizing Committee member, Program Committee member) |
| H. Asahi | 15th International Colloquium on Scanning Probe Microscopy (Publication Committee member)                       |
| H. Asahi | 15th International Conference on Molecular Beam Epitaxy (International Advisory Committee member)               |
| H. Asahi | Second International Symposium on Growth of III-Nitrides (International Advisory Committee member)              |
| H. Asahi | Journal of Crystal Growth (Editor)                                                                              |
| H. Asahi | J. Materials Science: Materials in Electronics (Editorial Board member)                                         |
| H. Asahi | Journal of Physics: Condensed Matter (Advisory Editorial Board member)                                          |
| H. Asahi | e-Journal of Surface Science and Nanotechnology (Advisory Board member)                                         |

#### **Publications in Domestic Meetings**

|                                      |          |
|--------------------------------------|----------|
| The Japan Society of Applied Physics | 9 papers |
| PASPS Symposium                      | 5 papers |
| Electronic Materials Symposium       | 1 paper  |

## **Sponsorship**

### **Grant-in-Aid for Scientific Research (B) (2)**

|          |                                                                                                                         |            |
|----------|-------------------------------------------------------------------------------------------------------------------------|------------|
| H. Asahi | Study on Room Temperature Ferromagnetic Nitride Semiconductor Nanostructures and Application to Nanospintronics Devices | ¥5,500,000 |
|----------|-------------------------------------------------------------------------------------------------------------------------|------------|

### **Grant-in-Aid for Scientific Research on Priority Areas**

|           |                                                                                           |            |
|-----------|-------------------------------------------------------------------------------------------|------------|
| H. Asahi  | Study on Fabrication of InN-Based Long Wavelength Circular Polarized Semiconductor Lasers | ¥3,700,000 |
| Y.K. Zhou | Experimental Study on Quantum Nanostructures of Insoluble Impurity Doped Semiconductors   | ¥3,000,000 |

### **Grant-in-Aid for Creative Scientific Research**

|          |                                                                                                     |             |
|----------|-----------------------------------------------------------------------------------------------------|-------------|
| H. Asahi | Development of properties and functionalities by precise control of rare-earth doping (Y. Fujiwara) | ¥30,420,000 |
|----------|-----------------------------------------------------------------------------------------------------|-------------|

## Department of Handai Multi-Functional Nanofoundry

|                                 |                                   |
|---------------------------------|-----------------------------------|
| Professor:                      | Tomoji KAWAI                      |
| Professor:                      | Seiichi TAGAWA                    |
| Professor:                      | Hirotarou MORI                    |
| Specially appointed researcher: | Akio TAKAOKA (Professor emeritus) |
|                                 | Hirotoishi FURUSHO (2007.5.1-)    |
|                                 | Naoko KAJIMURA                    |
|                                 | Tomoki NISHIDA (2007.7.1-)        |
|                                 | ChunLin CHEN (2007.8.16-)         |
|                                 | Lin-Yen LIN (2007.10.1-)          |
|                                 | Naoko YAMADA                      |
|                                 | Masakazu MURASUGI                 |
|                                 | Hideto OHNISHI(2007.10.16-)       |
|                                 | Yoshinori MATSUI (2007.4.1-4.30)  |
|                                 | Takahiro OHNO (2007.4.1-8.31)     |
|                                 | Osamu SUEKANE (2007.7.1-10.31)    |
| Supporting staff                | Yasuo NAKAMURA (2007.11.1-)       |
|                                 | Naomi YANAMORI (2007.12.17-)      |
|                                 | Norio SUNAGAWA                    |
|                                 | Keiko ENMI                        |
|                                 | Chie MATSUMOTO (2007.6.1-)        |

### Outlines

Handai Multi-Functional Nanofoundry was founded in Mission of Nanotechnology Network Japan, supported by Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. The purpose to start up the Nanofoundry is to establish a platform supporting Nanotechnology research and development, especially, for researchers outside of Osaka University. Nanofoundry started from April 2007, and our efforts resulted in supporting 79 research themes.

The Mission of Nanotechnology Network Japan was organized to respond to the requests that researchers belonging to public / private universities or companies hope to realize and to respond to researchers finding opportunity to use special facilities and equipments for their nanotechnology research and development program.

Institute of Science and Industrial Research (ISIR), Osaka University has played an important role in Nanotechnology fields by providing individual technologies and information. Our Nanofoundry supported lots of researchers outside of Osaka University through “Nanofabrication”, “Molecular and thin film fabrication” and “Characterization & analysis”.

Focuses of Handai Multi-Functional Nanofoundry are shown below.

- (1) Innovation by integrated and speedy nanotechnology support consisting of “Fabrication” “Observation ”and “Measurement”.
- (2) Creation of advanced interdisciplinary nanotechnology through integrated research and development of inorganic and organic materials, metals, semiconductor materials, and biomaterials.

- (3) Fostering of scientists in the field of advanced interdisciplinary nanotechnology.

## **Current Research Project**

### **Bring-up Handai Multi-Functional Nanofoundry**

The 79 research themes have been supported in this project in 2007. Considering they have been applied for by researchers in the universities, companies, and national institutes, we are able to see that Nanofoundry activates clearly nanotechnology field. Nanofoundry has been founded to support nanotechnology researchers through nanofabrication, molecular and thin film fabrication, characterization and analysis. These supports are divided into following four types. (a) Technical consulting, (b) Collaborative research, (c) equipment use, and (d) Technical supports.

### **Break-through toward Multi-functional Nanotechnology R&D**

Nanofoundry support advanced nanotechnology research and development as well as fundamental study. The research on functional integration and system building based on nanomaterials is acceptable in the Nanofoundry.

### **Fusion between Top-down and Bottom-up Nanotechnologies**

For Top-down and Bottom-up Nanotechnologies, a lot of useful equipments such as FIB, EB drawing and PLD, and so on, are in operation. The fusion between Top-down and Bottom-up Nanotechnologies will bring much important progress on nanotechnology in the near future.

## **Publications**

### **Original Papers**

Dielectric Properties of Ba(Zr,Ti)O<sub>3</sub> Thin Films Fabricated by Pulsed Laser Deposition, T.Hino, M. Nishida, T. Araki, T.Ohno, T. Kawahara, M. Murasugi, H. Tabata, T. Kawai: J. Laser Micro/Nanoengineering, 2 (3) (2007) 166-169.

### **International Conferences**

High-aspect-ratio micromachining of fluoropolymers using focused ion beam (poster), Y. Matsui, N. Miyoshi, A. Oshima, S. Seki, M. Washio, S. Tagawa: 2007 MRS Spring Meeting, USA, Apr. 10, 2007.

Direct etching process for nanofabrication of crosslinked PTFE using focused ion beam (poster), N. Fukutake, T. Urakawa, N. Miyoshi, A. Oshima, M. Washio, Y. Matsui, S. Seki, S. Tagawa: 9<sup>th</sup> TROMBAY SYMPOSIUM ON RADIATION & CHEMISTRY(TSRP2008), Pune, India, January 6-11,2008.

### **Publications in Domestic Meetings**

|                                         |         |
|-----------------------------------------|---------|
| Society of Polymer Science, Japan       | 1 paper |
| Japan Radioisotope Association          | 1 paper |
| Japanese Society of Radiation Chemistry | 1 paper |

## **Sponsorship**

### **Entrusted Research**

|          |                                                  |              |
|----------|--------------------------------------------------|--------------|
| T. Kawai | MEXT, Mission of Nanotechnology Network<br>Japan | ¥155,000,000 |
|----------|--------------------------------------------------|--------------|

## Open Laboratory

Professor (concurrent, manager): Yoichi YOSHIDA  
Professor (concurrent): Katsuaki SUGANUMA  
Professor (concurrent): Hidekazu TANAKA  
Technical Staff: Kimihiro NORIZAWA  
Supporting Staff: Kayoko OHASHI

## Outlines

Open Laboratory supports the comprehensive research for creative and advanced academic research on materials and devices, which should become the foundation of scientific and technological development on nanotechnology.

## Current Research Project

On 2007, the following 19 researchers used Open Laboratory for 22 projects.

|                               |                                                            |
|-------------------------------|------------------------------------------------------------|
| Prof. Yasufumi FUJIWARA       | Graduate School of Engineering                             |
| Prof. Kiichi FUKUI            | Graduate School of Engineering                             |
| Prof. Yoshihisa INOUE         | Graduate School of Engineering                             |
| Prof. Kazuyoshi ITOH          | Graduate School of Engineering                             |
| Prof. Tomoyuki KAKESHITA      | Graduate School of Engineering                             |
| Prof. Susumu KUWABATA         | Graduate School of Engineering                             |
| Prof. Ryoichi NAKATANI        | Graduate School of Engineering                             |
| Prof. Yusuke MORI             | Graduate School of Engineering                             |
| Prof. Kazuyoshi IKUTA         | Research Institute for Microbial Diseases                  |
| Prof. Naoyuki TANIGUCHI       | Research Institute for Microbial Diseases                  |
| Prof. Yoshimitsu YAMASAKI     | Graduate School of Medicine                                |
| Prof. Hirotaro MORI           | Research Center for Ultra-High Voltage Electron Microscopy |
| Prof. Shojiro NISHIO          | Promotion of Research on Nanoscience and Nanotechnology    |
| Prof. Tomoji KAWAI            | Institute of Scientific and Industrial Research            |
| Prof. Hikaru KOBAYASHI        | Institute of Scientific and Industrial Research            |
| Assoc. Prof. Shun'ichi KURODA | Institute of Scientific and Industrial Research            |
| Prof. Riichiro MIZOGUCHI      | Institute of Scientific and Industrial Research            |
| Prof. Seiichi TAGAWA          | Institute of Scientific and Industrial Research            |
| Prof. Hiroshi YOSHIDA         | Institute of Scientific and Industrial Research            |

## Radiation Laboratory

|                                           |                                                                                                                                |
|-------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|
| Professor, Director:                      | Tetsuro MAJIMA                                                                                                                 |
| Professors                                | Seiichi TAGAWA, Goro ISOYAMA, Yoichi YOSHIDA                                                                                   |
| Associate Professors:                     | Ryuko KATO, Yoshihide HONDA, Shu SEKI (until 2007.9.30),<br>Mamoru FUJITSUKA, Takahiro KOZAWA,<br>Kiyohiko KAWAI, Jinfeng YANG |
| Specially Appointed Associate Professors: | Masayuki ENDO                                                                                                                  |
| Research Associates:                      | Toshiji IKEDA, Norio KIMURA, Kazuo KOBAYASHI,<br>Sachiko TOJO, Shigeru KASHIWAGI, Akinori SAEKI,<br>Takashi TACHIKAWA          |
| Specially Appointed Research Associates:  | Masanori SAKAMOTO, Takafumi KONDO                                                                                              |
| Technical Staff:                          | Tamotsu YAMAMOTO (until 2007.7.20), Kumiko BABA (until<br>2007.7.20)                                                           |
| Support Staff:                            | Ritsuko NAGAO                                                                                                                  |

## Outline

The Radiation Laboratory was newly established in the fiscal year 2002 in the Nanoscience and Nanotechnology Center as a successor of the *Radiation Laboratory*, which was a facility directly attached to the Institute but had been reorganized to be part of the center, for operating experimental equipment previously owned by the *Radiation Laboratory*. The main pieces of the equipment are the 40 MeV L-band electron linear accelerator (linac), the 150 MeV S-band electron linac, the 40 MeV RF-gun electron linac, and the  $^{60}\text{Co}$   $\gamma$ -ray irradiation facility. Among them, the L-band linac and the  $\gamma$ -ray irradiation facility are open to users in Osaka University. The staff of the Radiation Laboratory is composed of the full-time members, who are two technicians from the Technical Division and a secretary, and concurrent members from the Division of Beam Science for Nanotechnology of the center and the Division of Beam Science and Technology as well as related Departments of the institute. They run the Radiation Laboratory and care for outside users.

## Achievement

### L-band linac

The L-band electron linac has four operation modes, which are transient, steady, single-bunch, and multi-bunch modes, in combination with either the short or long pulse duration of injected electrons and operation of the sub-harmonic buncher or not, and has ability to accelerate an electron beam up to the maximum energy 40 MeV and the highest charge per bunch 91 nC in the single bunch operation mode or the maximum current injected from the electron gun 30.6 A in the transient mode at the repetition rate 60 pulses per second at maximum. The machine time of the L-band linac in the fiscal year 2007 is as follows; 119 days including 18 days for maintenance are allocated in the first term and 119 days including 36 days for maintenance in the latter term. The operation days in the year are 195 days in total and the operation time is 2,240 hours. In



this fiscal year, in order to enhance stability of the electron beam in the single-bunch and the multi-bunch modes, we replaced three accelerating cavities for the sub-harmonic buncher system.

#### **S-band linac**

The S-band linac can accelerate an electron beam of the nominal energy 100 MeV and a peak current 0.2 A at the repetition rate 30 Hz, and it has been used for production of the slow positron beam.

#### **RF-gun linac**

The formal name of the RF-gun linac is the laser-photocathode S-band RF electron linac. It can accelerate a pico-second electron pulse beam to 40 MeV at maximum and can produce a short-pulse electron beam down to the femto-second region by means of the magnetic pulse compression method. These femto-second or pico-second pulse electron beams are mainly used for studies to investigate reactions induced by quantum beams. In this fiscal year, we operated the linac for 950 hours in eight months. The operation of the linac was satisfactory for the most part.

#### **$^{60}\text{Co}$ $\gamma$ -ray irradiation facility**

The  $^{60}\text{Co}$   $\gamma$ -ray irradiation facility is equipped with two irradiation rooms with different areas and irradiation experiments are conducted using three high-intensity  $^{60}\text{Co}$  sources. In this fiscal year, the facility was widely used not only by members of our institute but also by those coming from the Graduate School of Science, the Graduate School of Engineering, the Research Institute for Microbial Diseases, and the Faculty of Medicine. The number of research subjects increased compared with that in last year and the facility was extensively used over the university and the total utilization time is about 2520 hours, which is longer than a value in last year.

#### **Join-use**

The number of joint-use this fiscal year is 23 subjects from this institute, 14 subjects from other faculties and institutes of the university, and 5 subjects proposed by groups including members of other universities and institutes, and these are added up to 42 subjects in total.

We held two workshops; “New Development of the Radiation Laboratory and Beam Science” held on December 14, 2007, and “New Development of Chemistry using Beams” held on January 23, 2008. In addition, we held the annual meeting for presenting results obtained in the fiscal year 2007 on March 13, 2008 at the Joint-Project room of the institute. We received more than 200 visitors to the Radiation Laboratory.

#### **Radiation safety management**

The number of radiation users in ISIR is 156 persons in the fiscal year 2007. Education and training courses for the users was held on April 5, 6, 2007 at the MO Hall in the Convention Center of Osaka University. An education and training course for new users was held on April 23, 2007 at the Joint-Project room of the institute.

## **Electron Microscope Laboratory**

Professor, Director:        Yoshihiko HIROTSU

### **Outlines**

Electron microscope laboratory was established in 1951 and contributed to micro structural investigation in ISIR. From 2004 the facility belongs to the nano-science and nanotechnology center of ISIR and is supporting nanoscale structural observations and structure analyses of advanced nano-materials.

This laboratory has a 300 kV high-resolution analytical electron microscope with a field emission gun and a scanning electron microscope. These electron microscopes serve to make atomic scale structural observations, nano-area electron diffraction analyses, and nano-area chemical analyses of materials in response to each research division.

### **Achievement**

In the year of 2007, the 300 kV TEM served as an important equipment for the nano-structure characterization researches of 8 laboratories in ISIR with operation times as many as 384.

## **Electronic Processing Laboratory**

Professor: Hajime ASAH  
Associate Professor: Shigehiko HASEGAWA  
Associate Professor: Takuya MATSUMOTO  
Associate Professor: Koichi SUDOH  
Assistant Professor: Yi-Kai ZHOU  
Assistant Professor: Kenzo MAEHASHI

### **Outlines**

Electronic Processing Laboratory was established as a sort of device fabrication work-shop in 1991. The aim of this laboratory is to contribute to the development of nanotechnology and related researches by setting up the equipment and systems for fabrication, required commonly for the researches related to the areas such as photonic and electronic materials, molecular device materials and organic device materials and by improving process technology for various device materials.

The equipment and systems are a small-size clean room, a double crystal X-ray diffractometer, an atomic force microscope, a digital optical microscope, a photolithography system, a sputter deposition system, a high vacuum evaporation system, an electron beam evaporation system, a reactive ion etching system, a focused ion beam system, a crystal cleaving system, a wire bonding system and personal computers for data analysis

This laboratory is utilized for experimental researches of surface structure analysis and electrode formation, for the measurements of electronic and other properties of various materials and also for the fabrication of photonic, electronic and molecular devices. In the year of 2007, the equipment and systems were used over 310 times from 13 laboratories and facilities.

## **Nanofabrication Shop**

Director: Hiroyuki NOJI  
Technical Staffs: Kimiaki TANIHATA, Shouichi SAKAKIHARA,  
Takeshi ISIBASHI

### **Outlines**

Nanofabrication Shop was established in 2005 in order to promote nanotechnology-related research by use of equipments and special skills for nanotechnology researchers and students belonging to ISIR. In addition, this shop fabricates nano-devices for the ISIR researchers and develops devices for researchers who want to apply those devices for their own experiments.

### **Activities**

We created the environment for fabricating glass-masks by use of EB-lithography. Combining glass-masks with emulsion-masks made by reduced picture, we have covered all fabrication order of photolithography. In addition, we purchased rapid prototyping system which shapes photo-sensitive resin into steric objects. It enables us to do complicated three dimensional fabrications.

#### **On demand fabrication requests**

We have received requests from 8 laboratories in ISIR. Total number of their requests reached 57.

#### **Practice seminar of fabrication and application of micro-devices**

We have held a practice seminar. The content was making artistic objects utilizing micro-fabrication techniques. It took 1 day and was held 3 times. Total participants were 11 people.

#### **Participation in “nanotech 2007”**

We have made a poster exhibition and micro-devices demonstration in the booth of Nanotechnology Center in the international nanotechnology exhibition and conference “nanotech 2008” which was held on 13th to 15th of February in 2008.

## Materials Analysis Center

|                      |                                                         |
|----------------------|---------------------------------------------------------|
| Professor Director:  | Hiroaki SASAI                                           |
| Associate Professor: | Takeyuki SUZUKI                                         |
| Research Associate:  | Yoshio TAKAI                                            |
| Technical Staff:     | Hitoshi YAMADA<br>Takanori TANAKA<br>Tsuyoshi MATSUZAKI |
| Support Staff:       | Misayo IMAI                                             |

### Outlines

The Materials Analysis Center was founded in 1977, whose project includes (1) analysis of samples provided from other research sections in ISIR and (2) original research for developing novel synthetic methods using a molecular catalyst.

### Current Research Programs

#### Iridium-catalyzed oxidation: development and applications

Development of catalytic reaction using clean oxidant is one of the most important themes in modern organic synthesis. In addition, desymmetrization of *meso* diols is the efficient methods for the synthesis of chiral building blocks. This time we have developed the catalytic asymmetric synthesis for the key intermediate of ottelione and scyphostatin by using desymmetrization of *meso* diols, which are a potent antitumor and a inhibitor of sphingomyelinase. The appropriate selections of cooxidant, base, and protecting group are important to obtain high yield and selectivity in this reaction.

### Publications

#### Original Papers

Design and Synthesis of Chiral Hybrid Spiro (isoxazole-isoxazoline) Ligands, Koranne, P. S.; Tsujihara, T.; Arai, M. A.; Bajracharya, G. B.; Suzuki, T.; Onitsuka, K.; Sasai, H.: *Tetrahedron: Asymmetry*, 18 (2007) 919-923.

Enantioselective Total Synthesis of (+)-Ottelione A, (-)-Ottelione B, (+)-3-epi-Ottelione A and Preliminary Evaluation of Their Antitumor Activity, Araki, H.; Inoue, M.; Suzuki, T.; Yamori, T.; Kohno, M.; Watanabe, K.; Abe, H.; Katoh, T.: *Chem. Eur. J.*, 13 (2007) 9866-9881.

Enantioselective Glyoxylate-ene Reaction using a Novel Spiro Bis(isoxazoline) Ligand in Copper Catalysis, Wakita, K.; Bajracharya, G. B.; Arai, M. A.; Takizawa, S.; Suzuki, T.; Sasai, H.: *Tetrahedron: Asymmetry*, 18 (2007) 372-376.

#### International Conferences

Development of Dendritic Artificial Enzymes with Catechol Oxidase Activity (poster), Doss Jayaprakash, Rashid N. Nadaf, Takahiro Kawase, Takeyuki Suzuki, Hiroaki Sasai: 12th Asian Chemical Congress.

Development of Dendritic Artificial Enzymes with Catechol Oxidase Activity (poster), Rashid Nabisaheb Nadaf, Takahiro Kawase, Doss Jayaprakash, Takeyuki Suzuki and Hiroaki Sasai: 2nd Aachen-Osaka Joint Symposium: Green Sustainable Biological and Chemical Processes.

Development of Dendritic Artificial Enzymes with Catechol Oxidase Activity (poster), Doss Jayaprakash, Rashid N. Nadaf, Takahiro Kawase, Takeyuki Suzuki, Hiroaki Sasai: Chirality at the Nanoscale 2007.

**Publications in Domestic Meetings**

|                                       |          |
|---------------------------------------|----------|
| Symposium on Organometallic Chemistry | 1 paper  |
| Symposium on Organic Synthesis        | 1 paper  |
| The Chemical Society of Japan         | 3 papers |

**Sponsorship**

**Other Research Fund**

|                        |          |
|------------------------|----------|
| T. Suzuki    KRI Corp. | ¥300,000 |
|------------------------|----------|

# Materials Science & Technology Research Center for Industrial Creation (MSTeC)

## Outline

Materials Science & Technology Research Center for Industrial Creation (MSTeC) was founded in April 2005 for contributing to the creation of new industry through the complementary cooperation with Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. This center consists of two projects: P1 Materials Research Project and P2 Human Interface Research for Safety and Security Project which are divided to four groups: G1 Hard Materials Research Group, G2 Soft Materials Research Group, G3 Medical Sciences Research Group, and G4 Human Interface Research Group.

Director: Prof. H. Nakajima

P1 Materials Research Project

G1 Hard Materials Research Group: Group leader: Prof. H. Nakajima

G2 Soft Materials Research Group: Group leader: Prof. T. Majima

P2 Human Interface Research for Safety and Security Project

G3 Medical Sciences Research Group: Group leader: Prof. A. Yamaguchi

G4 Human Interface Research Group: Group leader: Prof. H. Yoshida

## Achievements

- Development of a new fabrication process for lotus-type porous metals without high pressure hydrogen gas
- Development of low temperature interconnection technology
- Fabrication of new lotus-type porous materials and its surface treatment
- Development of on-demand printing circuit technology with nanopaste
- Laser-induced functional chemistry and its application
- Synthesis and applications of chiral spiro ligands
- Self-assembled photofunctionalized biomolecules
- Development of practical synthetic route to chiral spiro compounds via a catalytic Asymmetric Reaction
- Three-dimensional microwiring technique using the two-laser beams with different wavelength
- Studies on structure, function, regulation and physiological functions of xenobiotic transporters
- The Research of new possibility of the radiation therapy
- Identification of the lipophilic cell signaling molecules transporter as a target for producing a new drug
- Dynamic optical modulation of the electron beam for newly high-performance intensity modulated radiation therapy

- Roles of xenobiotic transporters in cellular physiology
- Research on modeling and prediction of the industrial structure change
- Research on knowledge sharing technology for manufacturing support with safety, ease, and creation
- Musical Contents Generation from Sensor Data
- Research on cell processing devices / platform robot for the research implementation
- Research on the strategic new industry prediction accompanying change of industrial structure
- Reliability diagnosis for solid oxide fuel cells by acoustic emission measurement and machine learning



# Materials Research Project

## Outline

The Materials Research Project is composed of two groups with research fields: Hard Materials (such as metals, semiconductors and ceramics) and Soft Materials (such as organic molecules, polymers, and biomolecules). We actively make joint researches with Institute of Multidisciplinary Research for Advanced Materials in Tohoku University and private enterprises. The development of high-degree materials can be obtained by highly advanced processes with new functional materials and their characterization.

In Hard Materials Group, the purpose is to develop novel processing of porous materials which controlled by nanostructure, microstructure and shape design. In addition, this group focuses on the identification of interconnection process, and on the development of new materials for environmental electronics packaging.

In Soft Materials Group, the achievement of design, synthesis, assembly, and construction of functional organic molecules, polymers, and biomolecules is conducted for development of new functional molecules and materials based on elucidation of photoelectronic function, molecular recognition, catalytic reaction, high-ordered structure, and combination of multi-functions.

## Achievements

- Development of a new fabrication process for lotus-type porous metals without high pressure hydrogen gas
- Development of low temperature interconnection technology
- Fabrication of new lotus-type porous materials and its surface treatment
- Development of on-demand printing circuit technology with nanopaste
- Laser-induced functional chemistry and its application
- Synthesis and applications of chiral spiro ligands
- Self-assembled photofunctionalized biomolecules
- Development of practical synthetic route to chiral spiro compounds via a catalytic Asymmetric Reaction
- Three-dimensional microwiring technique using the two-laser beams with different wavelength

## Hard Materials Research Group

|                                 |                                   |
|---------------------------------|-----------------------------------|
| Professor:                      | Hideo NAKAJIMA, Katsuaki SUGANUMA |
| Designated Associate Professor: | Shunkichi UENO                    |
| Designated Research Associate:  | Keun-Soo KIM(2005.4.1-2007.10.15) |
| Graduate Students:              | Mitsuru KAWAZOME                  |

### Outlines

The main purpose of this department is to investigate physics of materials and develop novel processing of the materials. The department has undertaken the following several topics of the metallic materials science and engineering.

Lotus-type porous materials developed by this department are unique materials which exhibit extraordinary superior mechanical strength. The materials are fabricated by unidirectional solidification using gas solubility gap at their melting point. Main issues are to develop a new simple and safety fabrication process for lotus-type porous materials and to fabricate new lotus-type porous materials. In this year, we have established a simple fabrication process for porous metals using thermal-decomposition-compounds without high-pressure hydrogen gas and high-pressure vessel and fabricated lotus-type porous spinel under low hydrogen partial pressure.

We focus on the identification of interconnection process, and on the development of new materials for environmental electronics packaging. We are conducting the development of on-demand printing circuit technology with nanopaste, and of lead-free interconnection technology.

### Current Research Project

#### **1. Development of a new fabrication process for lotus-type porous metals without high-pressure hydrogen**

We developed a new fabrication process for lotus-type porous metals using thermal-decomposition-compounds without high pressure hydrogen gas and high-pressure vessel in this year. The fabrication cost of lotus-type porous metals for this process is a tithe of the hitherto known process using high pressure hydrogen gas and high-pressure vessel. The new process will be boosted an industrial application of lotus-type porous metals.

#### **2. Fabrication of a new lotus-type porous ceramics**

For the increasing use of the lotus-type porous ceramic, the fabrication of porous ceramics by unidirectional solidification were conducted using optical floating zone furnace. Lotus-type porous spinel was successfully prepared by the solidification under low hydrogen partial pressure. The porosity and pore diameter can be controlled by experimental conditions such as hydrogen partial pressure, total pressure, solidification rate, etc.

#### **3. Development of on-demand printing circuit technology with nanopaste**

Wring printing method is one of the key issues on fine patterning of circuits with

nanopastes. A variety of processes have potentials and each method has its own advantages. Ink-jet is one of major processes for electronics patterning. There are key technologies, i.e., control of Ag nanopaste suitable for wiring, ink-jet process suitable for fine pitch patterning, properties of patterned circuits and optimization, and practical applications. A new type of inks for wiring metallic Ag lines was developed. The inks are Ag carboxylate compounds designed to be decomposed at temperatures between 110 °C to 170 °C.

#### **4. Development of lead-free electronic packaging technology**

Establishment of lead-free plating technology and whisker countermeasures is one of the critical problems remaining to be solved for lead-free electronics packaging. A new approach to prevent the Sn whisker, by surface treatment on Sn plating, was proposed. Ni, Au and Pd layer with the thickness of 50nm or 200nm was deposited on typical Sn plating by flash-coating process. Comparing with pure Sn plating, Ni/Sn, Au/Sn and Pd/Sn plating is much stable against Sn whisker formation in room ambient environment. Ni/Sn, Au/Sn and Pd/Sn plating samples significantly suppressed the Sn whisker formation under the compressive stress condition.

### **Publications**

#### **Original Papers**

Fabrication of Lotus-type Porous Metals by Continuous Zone Melting and Continuous Casting Techniques, \*H. Nakajima, S.K. Hyun, S.K. Park and M. Tane: Materials. Science Forum, 539-543 (2007) 187-192.

Lotus-Type Porous Nickel-free Stainless Steel with High Temperature Nitriding, \* K. Alvarez, S.K. Hyun and H. Nakajima: Materials. Science Forum, 539-543 (2007) 756-76.

Fabrication of Lotus-type Porous Copper-Aluminum Alloy by Unidirectional Solidification in Hydrogen Atmosphere, \*S.K. Hyun, T. Awadu, T. Ikeda and H. Nakajima: Materials. Science Forum, 539-543 (2007) 1898-1902.

Fabrication of Lotus-type Porous Ni-(15, 28 and 31) at.% Al Alloys by Unidirectional Solidification in Hydrogen Atmosphere, \*S.K. Hyun, T. Ikeda and H. Nakajima: Materials. Science Forum, 544-545 (2007) 323-32.

Pore Morphology of Lotus-Type Porous Copper Fabricated by Continuous Casting Technique, \*J.S. Park, S.K. Hyun, M. Tane and H. Nakajima: Solid State Phenomena, 124-126 (2007) 1725-1728.

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Anisotropic Fusion Profile and Joint Strength of Lotus-type Porous Magnesium by Laser Fusion, \* T. Murakami, T. Tsumura, T. Ikeda, H. Nakajima and K. Nakata: Materials Science and Engineering A, 456 (2007) 278-285.

Effect of transference velocity and hydrogen pressure on porosity and pore morphology of lotus-type porous copper fabricated by continuous casting technique, \*J.S.Park, S.K.Hyun, S.Suzuki and H.Nakajima: Acta Materialia, 55 (16) (2007) 5646-5654.

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Studies on solder bump electromigration in Cu/Sn-3Ag-0.5Cu/Cu system, \*K. Yamanaka, Y. Tsukada, K. Suganuma: Microelectronics Reliability, 47 (8) (2007) 1280-1287.

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Sn-Zn low temperature solder, \*K. Suganuma, K.S. Kim: J. Materials Science: Materials in Electronics, 18 (1-3.) (2007) 121-127.

Microstructure development of mechanical-deformation-induced Sn whiskers, \*S. K. Lin, Y. Yorikado, J. Jiang, K.S. Kim, K. Suganuma, S.W. Chen, M. Tsujimoto, I. Yanada: J. Electronic Mater., 36 (12) (2007) 1732-1734.

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Corrosion and recession of mullite in water vapor environment, \*S. Ueno, T. Ohji and H.T. Lin: J. European Ceramics Society, 28 (2) (2008) 432-435.

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## **Review Papers**

Problems and countermeasures after RoHS regulation (In Japanese), K. Suganuma,

Engineering Materials, 55-2 (2007) 30-38.

World environmental legislations on electronics and vehicles (In Japanese), K. Suganuma, J. Japan Institute of Light Metals, 57-5 (2007) 210-217.

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### **Books**

Ink-jet Wiring of Fine Pitch Circuits with Metallic Nano Particle Inks, Applications & Materials of Inkjet Printer II (In Japanese, ed. by K. Takahasi), K. Suganuma, D. Wakuda, K. S. Kim, CMC Publications, (2007) 209-217.

Handbook of Lead-Free Soldering Technology and Materials (In Japanese), K. Suganuma (editor), Kogyo Chosakai Publishing, Inc.

### **Patents**

"Composition of coating body and use the same", H. Nakajima, S. Ueno, E. Kasai and N. Hayashi, P2007-077132

Further 3 patents

### **International Conferences**

Mechanical Properties of Lotus-type Porous Metals (invited), \*H. Nakajima, M. Tane, S.K. Hyun, H. Seki: International Union of Theoretical and Applied Mechanics (IUTAM) Symposium on Mechanical Properties of Cellular Materials.

New Fabrication Method for Lotus-Type Porous Metals and its Application (invited), \*H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Electrochemical Behavior of High Nitrogen Ni-free Austenitic Stainless Steels in L929 and Cell Culture Medium, \*K. Alvarez, S.K. Hyun, H. Nakajima, and S. Fujimoto: 211th Meeting of The Electrochemical Society.

Fabrication and Plastic Deformation Process of Lotus-type Porous Metals, \*S. Suzuki, J.-S. Park, S.K. Hyun, H. Utsunomiya, and H. Nakajima: International Workshop for R&D Clustering among China, Japan, Korea in Eco-materials Processing.

Fabrication of Lotus-type Porous Carbon-steel by Continuous Casting Technique in Nitrogen Atmosphere, \*K. Kashihara, S. Suzuki, S.K. Hyun, H. Yonetani, and H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Fabrication of Lotus-type Porous Magnesium by Continuous Casting Technique (poster), \*S.K. Hyun, S. Suzuki, and H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Plasma Braze Welding of Lotus-type Porous Copper (poster), \*T. Tsumura, H. Yanagino, S.K. Hyun, H. Nakajima, and K. Nakata: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Impact Properties of Lotus-type Porous Carbon Steel Measured by Instrumented Charpy Testing (poster), \*T. Kujime, S. K. Hyun, and H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Fabrication of Lotus-type Porous Al-Si by Continuous Casting Technique (poster), \*J.S. Park, S.K. Hyun, S. Suzuki, and H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Application of Lotus Type Porous Metal for an Air Bearing Spindle System (poster), \*Um, Y.S., Park, S.H., Nakajima, H., Yoon, J.H., Hur, B.Y.: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Prevention of Sn Whisker Formation by Surface Treatment of Sn Plating Part 2, \*K.S. Kim, S.S. Kim, S.K. Kim, K. Suganuma, M. Tsujimoto, I. Yanadaa: 137th TMS Annual Meeting & Exhibition.

Sn-Ag-Cu soldering reliability influenced by process atmosphere, \*A. Baated, J. Jiang, K.S. Kim, K. Suganuma, S. Huang, B. Jurcik, S. Nozawa, M. Ueshima: 9th International IEEE CPMT Symposium on High Density Design, Packaging and Microsystem Integration (HDP'07).

Evolution of Cu<sub>2</sub>O Micro/Nano-Protrusions on the Inner Wall of Lotus Copper by Ar Ion Irradiation (poster), \*S. Tukuda, S. Ueno, H. Nakajima, S. Tanaka: 7th Pacific Rim Conference on Ceramic and Glass Technology.

Fabrication of Lotus-type Porous Alumina with High Compressive Strength Using Unidirectional Solidification (poster), \*L.M. Lin, S. Ueno, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Effect of Molten Temperature on the Formation of Lotus-type Porous Silicon during Unidirectional Solidification (poster), \*S. Ueno, S.Y. Kim, H. Nakajima: 5th International Conference of Porous Metals and Metallic Foams (MetFoam2007).

Hot Corrosion Resistance of Stainless Steel with LaPO<sub>4</sub> Environmental Barrier Coating (poster), \*S. Ueno, H. Nakajima, N. Hayashi and E. Kasai: 1st International Conference on Science and Technology for Advanced Ceramics.

Hot Corrosion Resistance of Stainless Steel with LaPO<sub>4</sub> Coating (poster), \*S. Ueno, H. Nakajima, N. Hayashi, S. Romankov, S. Komarov and E. Kasai: 11th Sanken International Symposium.

Effect of Impurities on Formation of Pores in Porous Alumina during Unidirectional Solidification, \*S. Ueno, L.M. Lin and H. Nakajima: 9th International Symposium on Ecomaterials Processing & Design.

## **Contributions to International Conferences and Journals**

|             |                                                                                                                                  |
|-------------|----------------------------------------------------------------------------------------------------------------------------------|
| H. Nakajima | Fifth International Conference on Porous Metals and Metal Foaming Technology (MetFoam2007) (Organizing Committee Member)         |
| H. Nakajima | High Temperature Materials and Progress (Editorial Board)                                                                        |
| H. Nakajima | High Temperature Materials and Progress (Guest Editor)                                                                           |
| H. Nakajima | Advanced Engineering Materials (Guest Editor)                                                                                    |
| H. Nakajima | Materials Transactions (Guest Editor)                                                                                            |
| H. Nakajima | Diffusion and Defect Data (Editorial Advisory Board)                                                                             |
| H. Nakajima | Materials Science Foundations (Editorial Advisory Board)                                                                         |
| H. Nakajima | Fifth Pacific Rim International Conference on Materials (PRICM-5) (Organizing Committee Member)                                  |
| H. Nakajima | International Conference on New Frontiers of Process Science and Engineering in Advanced Materials (Organizing Committee Member) |
| H. Nakajima | 4 <sup>th</sup> International Conference on Diffusion in Solids and Liquids (Emeritus Organizing Committee Chairman)             |
| H. Nakajima | International Conference on Eco-Materials Processing and Design VIII (Editorial Advisory Board)                                  |
| H. Nakajima | International Conference on Diffusion in Materials (Editorial Advisory Board)                                                    |
| H. Nakajima | 2nd International Symposium on Cellular Metals for Structural and Functional Applications (Program Committee Member)             |
| H. Nakajima | International Conference on Advanced Structural Functional Materials Design (Organizing Committee Member)                        |
| H. Nakajima | First International Conference on Light Alloy technology and Application (Organizing Committee Member)                           |
| H. Nakajima | THERMEC International Conference on Advanced Materials (Editorial Advisory Board)                                                |
| K. Suganuma | TMS Annual Meeting, Committee of Phase Stability, Phase Transformation, and Reactive Phase Formation in Electronic Materials IV  |
| K. Suganuma | Electronic Components and Technology Conference (ECTC), Materials Processing Committee                                           |

### **Publications in Domestic Meetings**

|                                          |           |
|------------------------------------------|-----------|
| Japan Institute of Electronics Packaging | 5 papers  |
| Japan Institute of Metals                | 15 papers |
| High Temperature Society of Japan        | 1 paper   |
| Heat Transfer Society of Japan           | 1 paper   |

### **Sponsorship**

#### **Grant-in-Aid for Scientific Research (\*) (\*)**

|         |                                                                                                                   |          |
|---------|-------------------------------------------------------------------------------------------------------------------|----------|
| S. Ueno | Elucidation of formation mechanism of functionally designed porous ceramics and application for catalysis support | ¥650,000 |
|---------|-------------------------------------------------------------------------------------------------------------------|----------|



**Entrusted Research**

|             |       |                            |            |
|-------------|-------|----------------------------|------------|
| K. Suganuma | JEITA | Prevention of tin whiskers | ¥5,235,000 |
|-------------|-------|----------------------------|------------|

**Other Research Fund**

|             |           |                                                                                                   |             |
|-------------|-----------|---------------------------------------------------------------------------------------------------|-------------|
| K. Suganuma | Osaka TLO | Development of electronics information media using low temperature sinterable metal nanoparticles | ¥25,747,000 |
|-------------|-----------|---------------------------------------------------------------------------------------------------|-------------|

## Soft Materials Research Group

Professor: Tetsuro MAJIMA, Hiroaki SASAI  
Specially Appointed Associate Professor: Masayuki ENDO  
Specially Appointed Research Associate: Masanori SAKAMOTO,  
Kazuhiro TAKENAKA

### Outlines

Achievement of design, synthesis, assembly, and construction of functional organic molecules, polymers, and biomolecules is conducted for development of new functional molecules and materials based on elucidation of photoelectronic function, molecular recognition, catalytic reaction, high-ordered structure, and combination of multi-functions.

### Current Research Project

#### Creation of functional nano-scale biomaterials

We investigated the arrangement and integration of chromophores using the frames of DNA and proteins and interaction of chromophores incorporated selectively. We successfully obtained the DNA nanostructures which were extended to micro-meter scale using DNA building blocks including the crosslinked DNA and DNA tile system. We also constructed the self-assembled porphyrin structures using the TMV, and investigated the arrangement and energy transfer process. Using these self-assembled structures, we investigate the functional nano-materials, control of the structures and photophysical responses, and the photochemical and electrochemical properties.

#### In-situ photochemical fabrication of metal nanoparticle/polymer composite

The metal nanoparticle/polymer nanocomposites were fabricated using in-situ photochemical fabrication method. When gold and copper ions were simultaneously reduced by photochemically-produced ketyl radicals in a poly(vinyl alcohol) film, the core/shell structured Au/Cu bimetallic nanoparticles were formed. On the other hand, when co-existing gold and nickel ions were treated by the similar manner, nickel ion was not reduced by ketyl radical and adsorbed on the formed gold nanoparticle.

#### Asymmetric Oxidative Cyclization Catalyzed by Pd-SPRIX Complexes

We have developed asymmetric catalysis using our original chiral bis(isoxazoline) ligands with spiro[4.4]nonane skeleton (SPRIXs). Thus far it has been found that Pd(II)-SPRIX complexes are quite effective catalysts to promote enantioselective Wacker-type reactions. As an extension of their utility, efficient asymmetric synthesis of  $\gamma$ -butenolides and 2-pyrrolinones, which were valuable architectural platform for many biologically active substances, was examined. Pd(II)-SPRIX-catalyzed oxidative cyclization of  $\beta,\gamma$ -unsaturated carboxylic acids and  $\beta,\gamma$ -unsaturated amides afforded optically active  $\gamma$ -butenolides and 2-pyrrolinone derivatives, respectively. It is noteworthy that the known chiral ligands did not exhibit any accelerating effects in the above reactions.

#### Efficient Synthetic Method of Chiral Hybrid Spiro (Isoxazole-Isoxazoline) Ligands

Development of efficient synthetic method of novel chiral hybrid spiro (isoxazole-isoxazoline) ligands was accomplished. A variety of ligands were readily prepared by palladium-catalyzed coupling reactions of the key intermediate in which bromide was introduced to the 5-position on the isoxazole ring. Their utility as a chiral ligand was examined for palladium-catalyzed oxidative cyclization.

#### **Asymmetric Synthesis of Novel Spiro Bis(isoxazoline) Ligand**

Novel chiral spiro bis(isoxazoline) ligand was prepared without a tedious optical resolution. Diastereoselective intramolecular double nitrile oxide cycloaddition of the key dioxime derived from bis(2,2,2-trifluoroethyl) malonate and the enantiomerically pure alcohol gave the desired ligand.

#### **Catalytic Enantioselective Synthesis of Chiral Spiro lactams**

Enantioselective synthesis of spiro lactams via a palladium-catalyzed intramolecular double Buchwald–Hartwig amidation was investigated. The desired spiro lactams consisting of two 3,4-dihydroquinolinone moieties were obtained in an optically active form by reaction of 2,2-bis(2-bromobenzyl)malonamide derivatives in the presence of palladium catalyst precursor and chiral ligand. Furthermore, the resulting spiro lactams were converted into novel phase transfer catalysts bearing a spiro bis(1,2,3,4-tetrahydroquinoline) framework, which were expected to create effective chiral environment, by conventional synthetic methods such as electrophilic aromatic bromination and hydride reduction.

## **Publications**

### **Original Papers**

Single-Molecule Observation of DNA Charge Transfer, T. Takada, M. Fujitsuka, and T. Majima: *Proc. Nat. Acad. Sci. USA*, 104 (27) (2007) 11179-11183.

Intermolecular Electron Transfer from Excited Benzophenone Ketyl Radical, M. Sakamoto, X. Cai, S. S. Kim, M. Fujitsuka, and T. Majima: *J. Phys. Chem. A*, 111 (2) (2007) 223-229.

One-Electron Oxidation of Alcohols by the 1,3,5-Trimethoxybenzene Radical Cation in the Excited State during Two-Color Two-Laser Flash Photolysis, X. Cai, M. Sakamoto, M. Fujitsuka, and T. Majima: *J. Phys. Chem. A*, 111 (10) (2007) 1788-1791.

Bimolecular Hole Transfer from the Trimethoxybenzene Radical Cation in the Excited State, X. Cai, M. Fujitsuka, and T. Majima: *J. Phys. Chem. A*, 111 (22) (2007) 4743-4747.

Intramolecular Triplet Energy Transfer via Higher Triplet Excited State during Stepwise Two-color Two-laser Irradiation, Y. Oseki, M. Fujitsuka, M. Sakamoto, A. Sugimoto, and T. Majima: *J. Phys. Chem. A*, 111 (39) (2007) 9781-9788.

Electron Transfer from Axial Ligand to  $S_1$ - and  $S_2$ -Excited Phosphorus Tetraphenylporphyrin, M. Fujitsuka, D. W. Cho, S. Tojo, A. Inoue, T. Shiragami, M. Yasuda, and T. Majima: *J. Phys. Chem. A*, 111 (42) (2007) 10574-10579.

Electron Transfer from  $S_2$  and  $S_1$  States of Pentacoordinated Tetrapyrrole Macrocycles to Pyromellitic Diimide as an Axial Ligand, K. Harada, M. Fujitsuka, A. Sugimoto, and T. Majima: J. Phys. Chem. A, 111 (45) (2007) 11430-11436.

Hole Transfer in DNA and Photosensitized DNA Damage: Importance of Adenine Oxidation, K. Kawai, Y. Osakada, M. Fujitsuka, and T. Majima: J. Phys. Chem. B, 111 (9) (2007) 2322-2326.

Energy Levels of Oligothiophenes in the Higher Excited Triplet States, Y. Oseki, M. Fujitsuka, M. Sakamoto, X. Cai, and T. Majima: J. Phys. Chem. C, 111 (2) (2007) 1024-1028.

Fluorescence Properties of Si-linked Oligothiophenes, M. Fujitsuka, D. W. Cho, J. Ohishita, A. Kunai, and T. Majima: J. Phys. Chem. C, 111 (5) (2007) 1993-1998.

Design of Cyclic Reaction Driven by Two-Color Two-Photon Excitation, M. Sakamoto, S. S. Kim, M. Fujitsuka, and T. Majima: J. Phys. Chem. C (Lett.), 111 (19) (2007) 6917-6919.

Correction to "Acceleration and Deceleration of Laser Induced Formation of Gold Nanoparticles in a PVA Film", M. Sakamoto, T. Tachikawa, M. Fujitsuka, and T. Majima: Langmuir, 23 (14) (2007) 7886-7886.

Donor-Acceptor Substituted Tetrakis(phenylethynyl)benzenes as Emissive Molecules during Pulse Radiolysis in Benzene, S. Samori, S. Tojo, M. Fujitsuka, E. L. Spitler, M. M. Haley, and T. Majima: J. Org. Chem., 72 (8) (2007) 2785-2793.

Relationship between Charge Transfer and Charge Recombination Determines Photocurrent Efficiency through DNA Films, T. Takada, C. Lin, and T. Majima: Angew. Chem. Int. Ed., 46 (35) (2007) 6681-6683.

Hole transfer rates in A-from DNA/2'-OMeRNA hybrid, K. Kawai, Y. Osakada, A. Sugimoto, M. Fujitsuka, and T. Majima: Chem. Eur. J., 13 (8) (2007) 2386-2391.

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Porphyrin Light-Harvesting System Constructed in the Tobacco Mosaic Virus Scaffold, M. Endo, M. Fujitsuka, and T. Majima: Chem. Eur. J., 13 (31) (2007) 8660-8666.

Photochemical Formation of Au/Cu Bimetallic Nanoparticles with Different Shapes and Sizes in a PVA Film, M. Sakamoto, T. Tachikawa, M. Fujitsuka, and T. Majima: Adv. Funct. Mater., 17 (6) (2007) 857-862.

Spin-correlated radical pairs in the synthetic hairpin DNA, S. Nakajima, K. Akiyama, K. Kawai, T. Takada, T. Ikoma, T. Majima, and S. Tero-Kubota: ChemPhysChem, 8 (4)

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Fabrication of Chromophore-Functionalized Gold Nanoparticles-Poly(Vinyl alcohol) Thin Film Nanocomposite: New Coordination Method using the Ni(II)-Nitrilotriacetic acid Complex Formation, M. Sakamoto, T. Tachikawa, Sung Sik Kim, M. Fujitsuka, and T. Majima: *ChemPhysChem*, 8 (11) (2007) 1701-1706.

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“SNP detection method by DNA single molecule fluorescence measurement based on DNA charge transfer”, T. Majima, T. Takada, K. Kawai, M. Fujitsuka, No. 2007-6829.

“Preparation of metal nanoparticles in matrices”, T. Majima, M. Sakamoto, M. Fujitsuka, No. 2007-28166.

“Preparation of modified metal nanoparticles and its method”, T. Majima, M. Sakamoto, M. Fujitsuka, No. 2007-095031.

### **International Conferences**

#### **International Conferences**

Charge Transfer in DNA (invited), T. Majima: 2007 Photochemistry Gordon Research Conference, Bryant University, Smithfield, Rhode Island, USA, July 8-13, 2007.

Mechanistic Insight into the  $\text{TiO}_2$  Photocatalytic Reactions (invited), T. Majima: 23th International Conference on Photochemistry, Cologne, Germany, July 29-Aug. 3, 2007.

Rapid Energy Migration along Photofunctional Polymers (poster), M. Fujitsuka and \*T. Majima: 23th International Conference on Photochemistry, Cologne, Germany, July 29-Aug. 3, 2007.

Charge Separation via Rapid Hole Transfer through Adenine-Hopping (poster), T.



Takada, K. Kawai, M. Fujitsuka, and \*T. Majima: 23th International Conference on Photochemistry, Cologne, Germany, July 29-Aug. 3, 2007.

One-electron oxidation of organic compounds during TiO<sub>2</sub> photocatalytic reactions (invited), \*T. Tachikawa and T. Majima: Langmuir Symposium 2007 in Osaka University, Suita, Japan, Oct. 9, 2007.

Photochemical synthesis of metal nanoparticles in a PVA film (invited), \*M. Sakamoto and T. Majima: Langmuir Symposium 2007 in Osaka University, Suita, Japan, Oct. 9, 2007.

Development of New TiO<sub>2</sub> Photocatalysts (invited), T. Majima: 7th Pacific Rim Conference on Ceramic and Glass Technology, Shanghai, Nov. 11-14, 2007.

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Development of New TiO<sub>2</sub> Photocatalyst: Mechanistic Study of TiO<sub>2</sub> Photocatalytic Reactions (invited), T. Majima: The 9th International Symposium on Eco-materials Processing and Design, Changwon Exhibition Convention Center, Changwon, Korea, Jan. 7-9, 2008.

Photoinduced Charge Separation in Titania Nanotubes (poster), \*T. Tachikawa, S. Tojo, M. Fujitsuka, T. Sekino, and T. Majima: The 9th International Symposium on Eco-materials Processing and Design, Changwon Exhibition Convention Center, Changwon, Korea, Jan. 7-9, 2008.

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Charge Separation in Acridine Modified DNA (poster), \*K. Kawai, M. Fujitsuka, and T. Majima: 11th Sanken International Symposium / 6th nanotechnology center international symposium / 1st MSTEC international symposium, Awaji, Japan, Feb. 4-5, 2008.

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Design of Cyclic Reaction Driven by the Two-color Two-photon Excitation (poster), M. Sakamoto, M. Fujitsuka and \*T. Majima: 11th Sanken International Symposium / 6th nanotechnology center international symposium / 1st MSTEC international symposium, Awaji, Japan, Feb. 4-5, 2008.

Molecular Excitation Chemistry of Supramolecules and Nanomaterials, T. Majima: International Symposium on "New Trend in Chemistry of Supramolecules and Nanomaterials 2008", Osaka University, Japan, Feb. 6, 2008.

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Photophysical Properties of 1,8-Naphthalimide-linker-phenothiazine Dyads in Non-polar Solvents, \*D. W. Cho, M. Fujitsuka, and T. Majima: International

Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

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Single-Molecule Observation of DNA Charge Transfer, \*T. Takada, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Porphyrin Light-Harvesting System Constructed in the Tobacco Mosaic Virus Scaffold, \*M. Endo, M. Fujitsuka, and T. Majima: International Symposium on “New Trend in Chemistry of Supramolecules and Nanomaterials 2008”, Osaka University, Japan, Feb. 6, 2008.

Higher Excited State Chemistry for Light-Energy Conversion (invited), M. Fujitsuka and \*T. Majima: The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science, Daejeon, Korea, Feb. 27-28, 2008.

DNA Devices Based on Charge Transfer in DNA (invited), T. Majima: The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science, Daejeon, Korea, Feb. 27-28, 2008.

Development of New Catalytic Enantioselective Reactions Promoted by Pd(II)-Spiro Bis(isoxazoline) Complexes (poster), \*G. B. Bajracharya, P. S. Koranne, M. L. Patil, C. V. L. Rao, T. Tsujihara, S. Takizawa, T. Suzuki, H. Sasai: 19th French-Japanese Symposium on Medicinal and Fine Chemistry (FJS-2007), Toyama, Japan, May 13-16, 2007.

Pd(II)-SPRIX-Catalyzed Enantioselective Intramolecular Cyclizations (poster), \*G. B. Bajracharya, M. L. Patil, P. S. Koranne, C. V. L. Rao, T. Tsujihara, T. Suzuki, H. Sasai: 14th IUPAC Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS 14), Nara, Japan, August 2-6, 2007.

Development of Dendritic Artificial Enzymes with Catechol Oxidase Activity (poster),

D. Jayaprakash, \*R. N. Nadaf, T. Kawase, T. Suzuki, H. Sasai: 12th Asian Chemical Congress, Kuala Lumpur, Malaysia, August 22-25, 2007.

Development of Dendritic Artificial Enzymes with Caetchol Oxidase Activity (poster), \*D. Jayaprakash, R. N. Nadaf, T. Kawase, T. Suzuki, H. Sasai: Chirality at the Nanoscale, Barcelona, Spain, September 17-21, 2007.

Development of New Catalytic Enantioselective Reactions Promoted by Pd(II)-Spiro Bis(isoxazoline) Complex (poster), G. B. Bajracharya, P. S. Koranne, M. L. Patil, C. V. L. Rao, T. Tsujihara, S. Takizawa, T. Suzuki, \*H. Sasai: Chirality at the Nanoscale, Barcelona, Spain, September 17-21, 2007.

Development of New Catalytic Enantioselective Reactions Promoted by Pd(II)-Spiro Bis(isoxazoline) Complexes (poster), \*Y. Tanigaki, G. B. Bajracharya, P. S. Koranne, C. V. L. Rao, M. L. Patil, T. Tsujihara, K. Takenaka, S. Takizawa, K. Onitsuka, H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Development of Novel Chiral Spiro-type Ligands (poster), \*S. Nakatsuka, T. Nagano, P. S. Koranne, K. Takenaka, S. Takizawa, T. Suzuki, K. Onitsuka, H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Development of Dendritic Artificial Enzymes with Catechol Oxidase Activity (poster), \*R. N. Nadaf, D. Jayaprakash, T. Kawase, R. K. M. Gabr, S. Hashimoto, M. Mikami, T. Suzuki, H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Development of Dendritic Artificial Enzymes with Catechol Oxidase Activity (poster), \*S. Hashimoto, R. N. Nadaf, D. Jayaprakash, T. Kawase, G. R. K. Mohamed, M. Mikami, T. Suzuki, H. Sasai: 11th Sanken, 6th Nanotechnology Center, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Bifunctional Chiral Organocatalysts for the Enantioselective aza-Morita-Baylis-Hillman Reaction, \*H. Sasai: 21st International Congress for Heterocyclic Chemistry, Sydney, Australia, July 15-20, 2007.

Development of Bifunctional Organocatalysts for Enantioselective Aza-Morita-Baylis-Hillman Reaction (invited), \*H. Sasai: First International Conference on Advanced Organic Synthesis Directed toward the Ultimate Efficiency and Practicability, International Conference on Asymmetric Organocatalysis, Otsu, Japan, May 28-29, 2007.

Novel Enantioselective Reactions Promoted by Pd(II)-SPRIX Catalyst (invited), \*H. Sasai: International Chemical Conference (ICCT-2007), Hsinchu, Taipei, December 13-16, 2007.

Dual Activation in Oxidative Coupling of 2-Naphthols Catalyzed by Chiral Dinuclear

Vanadium Complexes (invited), \*H. Sasai: Post-symposium of ICCT-2007, Hsinchu, Taipei, December 17, 2007.

Dual Activation Catalysis (invited), \*H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Regio- and Enantioselective O-Allylation of Phenol and Alcohol Catalyzed by Planar-Chiral Cyclopentadienyl-Ruthenium Complex (poster), \*K. Onitsuka, H. Okuda, C. Kameyama, H. Sasai: 14th IUPAC Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS 14), Nara, Japan, August 2-6, 2007.

Development of New Catalytic Asymmetric Reaction Using Helical Polymer (poster), \*Y. Itano, K. Onitsuka, H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Asymmetric Catalysis of Planar-Chiral Cyclopentadienyl-Ruthenium Complexes: Regio- and Enantioselective Allylic Substitutions (poster), \*K. Onitsuka, H. Okuda, C. Kameyama, H. Sasai: 11th Sanken, 6th Nanotechnology Center, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Design of Novel Helical Polymer Ligands and Their Application to Asymmetric Diels-Alder Reaction (poster), \*K. Onitsuka, Y. Itano, H. Sasai: 11th Sanken, 6th Nanotechnology Center, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

Synthesis of Optically Active Spiro Compounds via Palladium-catalyzed Asymmetric Amidation (poster), \*N. Itoh, K. Takenaka, H. Sasai: Green Sustainable Biological and Chemical Processes, Osaka, Japan, November 15-17, 2007.

Synthesis of Optically Active Spiro Compounds via Palladium-catalyzed Asymmetric Amidation (poster), \*N. Itoh, K. Takenaka, H. Sasai: 11th Sanken, 6th Nanotechnology Center, 1st MSTEC International Symposium, Awaji, Japan, February 4-5, 2008.

#### **Contributions to International Conferences and Journals**

|           |                                                                                                                        |
|-----------|------------------------------------------------------------------------------------------------------------------------|
| T. Majima | 2007 KOREA-JAPAN Symposium on Frontier Photoscience (Conference Chair)                                                 |
| T. Majima | Symposium on "Beam-induced Chemistry of Supramolecules and Nanomaterials 2007 (Conference Chair)                       |
| T. Majima | Langmuir Symposium 2007 in Osaka University (Conference Chair)                                                         |
| T. Majima | The 9 <sup>th</sup> International Symposium on Eco-materials Processing and Design (Organizing Committee)              |
| H. Sasai  | 14th IUPAC Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS 14), (Organizing Committee) |

**Publications in Domestic Meetings**

|                                              |           |
|----------------------------------------------|-----------|
| Japan Photobiology and Photomedicine Meeting | 2 papers  |
| Photochemistry Meeting                       | 11 papers |
| Polymer Meeting                              | 1 papers  |
| Japan Chemical Society Meeting               | 10papers  |
| The Chemical Society of Japan                | 13 paper  |
| Symposium on Organic Reaction                | 2 papers  |
| Symposium on Organometallic Chemistry        | 1 paper   |
| Symposium on Organic Synthesis               | 1 paper   |

**Sponsorship****Grand-in-Aid for Scientific Research (S)**

|           |                                        |             |
|-----------|----------------------------------------|-------------|
| T. Majima | Nanoscience of Photofunctionalized DNA | ¥10,920,000 |
|-----------|----------------------------------------|-------------|

**Grand-in-Aid for Basic Scientific Research**

|           |                                                                                                                           |            |
|-----------|---------------------------------------------------------------------------------------------------------------------------|------------|
| T. Majima | Construction of devices for photoelectronic conversion using photochemical control of Tobacco Mosaic Virus supramolecules | ¥1,800,000 |
|-----------|---------------------------------------------------------------------------------------------------------------------------|------------|

**Grant-in-Aid for Scientific Research on Priority Areas**

|          |                                                              |            |
|----------|--------------------------------------------------------------|------------|
| H. Sasai | Development of Chiral Organocatalyst with Synergistic Effect | ¥2,300,000 |
|----------|--------------------------------------------------------------|------------|

**Entrusted Research**

|           |                                     |                                                                                                             |            |
|-----------|-------------------------------------|-------------------------------------------------------------------------------------------------------------|------------|
| T. Majima | IDEC Co.                            | Selection of plastic by laser light                                                                         | ¥1,690,000 |
|           | Satake Co.                          |                                                                                                             |            |
| H. Sasai  | Japan Science and Technology Agency | Preparation of Novel Medicinal Intermediates Based on Enantioselective Reactions Using Chiral Spiro Ligands | ¥2,600,000 |

**Grand-in-Aid for Scientific Research (C)**

|         |                                                                        |          |
|---------|------------------------------------------------------------------------|----------|
| M. Endo | Photofunctionalization of Apoptosis-related Enzymes for Cancer Therapy | ¥900,000 |
|---------|------------------------------------------------------------------------|----------|

**Grand-in-Aid for Encouragement of Young Scientists**

|             |                                                                                                                |            |
|-------------|----------------------------------------------------------------------------------------------------------------|------------|
| M. Sakamoto | Research for the fabrication of three-dimensional metal nanoparticle array using the two-color two-laser beams | ¥3,100,000 |
|-------------|----------------------------------------------------------------------------------------------------------------|------------|

**Other Research Fund**

|           |            |                                                                             |            |
|-----------|------------|-----------------------------------------------------------------------------|------------|
| T. Majima | TOYOTA Co. | Hydrogen absorbing alloys with high surface area produced by photoreduction | ¥5,989,000 |
|-----------|------------|-----------------------------------------------------------------------------|------------|

|           |                                       |                                                                         |            |
|-----------|---------------------------------------|-------------------------------------------------------------------------|------------|
| T. Majima | Sekisui Chemicals Co.                 | Super hydrophilicity by TiO <sub>2</sub> photocatalytic reaction        | ¥999,000   |
| T. Majima | Matsushita Electric Industrial Co.    | Study on highly reactive nanostructured TiO <sub>2</sub> photocatalysts | ¥1,732,000 |
| T. Majima | Mitsubishi Chemical Co.               | Basic research on chemical reaction via higher excited states           | ¥2,000,000 |
| H. Sasai  | Hosokawa Powder Technology Foundation | Development of Efficient Synthetic Methods for Functional Nanoparticles | ¥1,000,000 |
| H. Sasai  | Meiji Seika Kaisha                    |                                                                         | ¥1,000,000 |
| H. Sasai  | Daiso Co.                             |                                                                         | ¥600,000   |
| H. Sasai  | Nissan Chemical Industries            |                                                                         | ¥400,000   |
| H. Sasai  | Nagase ChemteX Co.                    |                                                                         | ¥200,000   |

# Human Interface Research for Safety and Security Project

## Outline

Human Interface Research for Safety and Security Project is one of two main projects of Materials Science & Technology Research Center for Industrial Creation, MSTeC, which is the newly established cooperative organization with ISIR and the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University from 2005. This project aimed for developing the sustainable technology of human interface for safety and security. This project contains two groups: 1) medical sciences research group and 2) human interface research group. Main research subjects are xenobiotic exporters as novel drug targets, next generation intensity modulated radiation therapy, novel sensors and software systems. In addition, we also investigate new industrial prediction tools.

## Achievements

- Identification of the exporters that mediates secretion of lipophilic signal transducing molecules.
- Roles of xenobiotic transporters in cellular physiology.
- The Research of new possibility of the radiation therapy
- Dynamic optical modulation of the electron beam for newly high-performance intensity modulated radiation therapy
- Research on bio-applications of novel nano structures and on integrated operation of the interfaces.
- Research on knowledge sharing technology for manufacturing support with safety, ease, and creation
- Research on the strategic new industry prediction accompanying change of industrial structure and success factors for high tech. venture companies.
- The adaptive interface by the sensor network and machine learning.



## Medical Sciences Research Group

Professor: Akihito YAMAGUCHI, Yoichi YOSHIDA

Specially Appointed-

Assistant Professor: Tsuyoshi NISHI, Takafumi KONDOH,  
Kunihiko NISHINO(2007.4.1.-2007.5.31.)

### Outlines

The main research objective of our group is understands the mechanism of basic biological processes that are important for normal cellular functions. Especially we are focusing on the transporters that are contributing the secretion of the lipid mediators to develop the transporter oriented drugs and are trying to understand the physiological roles of the xenobiotic transporters. We are also focusing on the development of the beam modulation technology about high spacial resolution and high speed control by a photo cathode RF gun for new high-performance radiation cancer therapy, development of the femtosecond pulse radiolysis observing ultra-fast radiation induced reaction in the human body to search for new possibility of the radiation therapy, and the theoretical study of a new irradiation effect by the ultimate short pulse radiation.

### Current Research Programs

#### **Characterization of the lipophilic signal transducing molecules export system in the mammalian cells.**

Intercellular signal transduction is the important system for the cell- cell communication in the highly organized living organism. Lipophilic compounds such as steroid hormones and lipid mediators are one of the most popular signaling molecules. However, little is known about how are these molecules exported from the cells. We are trying to identify the secretion mechanism and to isolate the transporters that are directly transporting these lipophilic molecules. For this purpose, we are focusing to identify the sphingosine-1-phosphate (S1P) secretion system from the platelet. S1P is the lipid mediators that are playing important roles in cell migration, proliferation and apoptosis. So far, we were identified that S1P is located in the inner leaflet of the plasma membrane and is showed thrombin or  $\text{Ca}^{2+}$  dependent secretion from the platelet. Using the transporter specific inhibitors, we proposed that ABC A-type transporters might participate the export of sphingosine-1-phosphate. Among the ABCA type transporters, we showed that ABCA7 is predominantly expressed in platelet. These results suggested that ABCA7 should be a candidate of sphingosine-1-phosphate transporter. We also identified that erythrocyte synthesize the S1P and S1P is secreted from the cell without any stimuli. We prepared the inside-out membrane vesicle from rat erythrocyte and success to measure the S1P transport activity. This S1P transport was ATP dependent manner and inhibited with glyburide and vanadate but not with other inhibitors for transporters or ionophores. These results strongly suggested the presence of transporter mediated S1P export system in rat erythrocyte.

#### **The Research of new possibility of the radiation therapy:**

The new possibility of the radiation cancer therapy was researched. Femtosecond pulse radiolysis system with a laser photo cathode RF gun LINAC in the ISIR is developed

for observation of the ultra-fast radiation induced chemical reaction in similar situation of human body. The original ion pulse radiolysis system is developed to elucidate induced effects by the different radiation rays such as the heavy ion beam and the proton beam. By the latest study, the new therapy principle was studied theoretically as a collective ionization by the ultimate short pulse radiation.

### **Dynamic optical modulation of the electron beam for newly high-performance intensity modulated radiation therapy**

For reduction of exposure dose to the normal tissue and to realize more safety and effective cancer therapy, and optical modulation technology of the electron beam was developed for new high-performance intensity modulated radiation therapy by a laser photo cathode RF gun LINAC of the ISIR. The dynamic optical modulation of the electron beam was studied toward synchronization to the breathing and involuntary muscle movement in the radiation therapy. A digital micro mirror device was used to advancement of the optical modulation and computer control of the visible laser light was succeeded in.

## **Publications**

### **Original Papers**

Tissue specific expression of the splicing variants of the mouse vacuolar proton-translocating ATPase a4 subunit, S. Kawasaki-Nishi, A. Yamaguchi, M. Forgac, T. Nishi: *Biochem. Biophys. Res. Commun.*, 364 (2007) 1032-1036.

The AraC-family regulator GadX enhances multidrug resistance of *Escherichia coli* by activating expression of the *mdtEF* multidrug efflux genes, K. NishinoY. Senda and A. Yamaguchi: *Journal of Infection and chemotherapy*, 14 (1) (2008) 23-29.

Identification of a spermidine excretion protein complex (MdtII) in *Escherichia coli*, K. Higashi, H. Ishigure, R. Demizu, T. Uemura, K. Nishino, A. Yamaguchi, K. Kashiwagi and K. Igarashi: *Journal of Bacteriology*, 190 (2) (2008) 872-878.

Regulation of multidrug efflux systems involved in multidrug and metal resistance of *Salmonella enterica* serovar Typhimurium, K. Nishino, E. Nikaido and A. Yamaguchi: *Journal of Bacteriology*, 189 (24) (2007) 9066-9075.

Bunch Length Measurement using Spectral Width of Monochromatic Synchrotron Radiation, A. Ogata, T. Kondoh, J. Yang, A. Yoshida and Y. Yoshida: *Nucl. Instr. and Meth. A*, 578 (2007) 348-350.

LWFA of Atto-Second Bunches for Pulse Radiolysis, A. Ogata, T. Kondoh, J. Yang, A. Yoshida and Y. Yoshida: *Int. J. Modern. Phys.*, 21 (2007) 447-458.

### **Review Papers**

Molecular mechanism of multi-drug efflux protein, A. Yamaguchi: *Infection, Inflammation, Immunity*, 37 (2007) 106-115.

Structural basis of xenobiotic recognition by a bacterial xenobiotic exporter, S.

Murakami and A. Yamaguchi: The Journal of Biochemistry, 79 (2007) 542-549.

### **Patents**

Modulator for the receptor of autoinducer-2, N. Kato, M. Hiraoka, J. Ohkanda, T. Kawano, A. Yamaguchi, K. Nishino, S. Ebisu and Bonnie L. Bassler, tokugan2007-056450

### **International Conferences**

Tissue and cellular localization of mouse ABCA5 proteins (poster), \*M. Ohigashi, T. Nishi, A. Yamaguchi: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium.

Thrombin stimulates S1P release from platelet-like particles derived from MEG-O1 cells (poster), \*Y. Hisano, T. Nishi, A. Yamaguchi: 11th Sanken International Symposium, 6th Nanotechnology Center International Symposium, 1st MSTEC International Symposium.

Roles of multidrug efflux pumps in antimicrobial peptide resistance of *Salmonella enterica*, \*T. Nakano, K. Nishino and A Yamaguchi: Florence Conference on Phenotype MicroArray Analysis of Microorganisms (19-21 Mar. 2008, Florence, Italy).

Regulatory network of AcrAB multidrug efflux pump in *Salmonella* and its role in response to metabolites, \*E. Nikaido, K. Nishino and A Yamaguchi: Florence Conference on Phenotype MicroArray Analysis of Microorganisms (19-21 Mar. 2008, Florence, Italy).

Physiological functions of bacterial multidrug efflux pumps (invited), \*K. Nishino and A Yamaguchi: The 3rd CNU-SANKEN Joint Symposium on Advanced Materials Science (27-28 Feb. 2008, Chungnam National University, Korea).

Structural Basis of Bacterial Multidrug Export, \*A Yamaguchi: 11<sup>th</sup> Sanken International Symposium/6th nanotechnology center international symposium/1st MSTEC international symposium(4-5 Feb. 2008, Hyogo).

Roles of indole signaling and intercellular signal transduction on type III secretion system-dependent pathogenicity in EHEC, \*H. Hirakawa, T. Kodama, T. Honda and A Yamaguchi: 3<sup>rd</sup> ASM Conference on Cell-Cell Communication in Bacteria (7-10 Oct. 2007, Texas, USA).

Visualization of *Escherichia coli* AcrAB-TolC efflux pump activity using ultra small chambers (poster), \*Y. Matsumoto, K. Nishino, R. Iino, S. Sakakihara, M. Nakata, H. Nojii and A Yamaguchi: 47<sup>th</sup> Interscience Conference on Antimicrobial Agents and Chemotherapy (Sep. 17-20, 2007, McCormick Place, Illinois USA).

Novel Aspects of Mechanisms of Antibacterial Resistance Revealed by Crystal Structure (invited), \*A Yamaguchi: 47<sup>th</sup> Interscience Conference on Antimicrobial Agents and Chemotherapy (Sep. 17-20, 2007, McCormick Place, Illinois USA).

Regulatory network of multidrug transporters reveals their physiological role in *Salmonella* virulence, \*K. Nishino, E. Nikaido, H. Sakata, T. Nakano, M. Tanaka and A Yamaguchi: 7<sup>th</sup> The Awaji International Forum on Infection and Immunity (Sep. 1-5, 2007, Awaji Yumebutai International Conference Center).

Regulatory network of multidrug transporters reveals their physiological role in *Salmonella* virulence (poster), \*K. Nishino, E. Nikaido, H. Sakata, T. Nakano, M. Tanaka and A Yamaguchi: 7<sup>th</sup> The Awaji International Forum on Infection and Immunity (Sep. 1-5, 2007, Awaji Yumebutai International Conference Center).

Regulation mechanisms of the *acrAB* multidrug efflux pump in *Salmonella enterica* in response to bacterial metabolites (poster), \*E. Nikaido, K. Nishino and A Yamaguchi: 7<sup>th</sup> The Awaji International Forum on Infection and Immunity (Sep. 1-5, 2007, Awaji Yumebutai International Conference Center).

Single Cell Measurement of Bacterial Drug Efflux in Femtoliter Chamber Array (poster), \*K. Nishino, R. Iino, M. Nakata, Y. Matsumoto, E. Nikaido, S. Sakakihara, S. Takeuchi, A Yamaguchi and H. Noji: American Society of Microbiology, 107th General Meeting, (May 21-25, 2007, Metro Toronto Convention Center, Toronto, Canada).

Metabolites of *Escherichia coli* Induce the Expression of Multidrug Efflux Pumps in *Salmonella enterica* (poster), \*E. Nikaido, K. Nishino and A Yamaguchi: American Society of Microbiology, 107th General Meeting, (May 21-25, 2007, Metro Toronto Convention Center, Toronto, Canada).

Dynamic Optical Modulation of the Electron Beam for the High Performance Intensity Modulated Radiation Therapy (poster), \*T. Kondoh, H. Kashima, J. Yang and Y. Yoshida: Proceedings of the Particle Accelerator Conference 2007.

Simulation Study on Attosecond Electron Bunch Generation (poster), \*K. Kan, T. Kondoh, J. Yang, Y. Yoshida: Proceedings of the Particle Accelerator Conference 2007.

Femtosecond Electron Beam Dynamics in Photocathode Accelerator (poster), \*J. Yang, K. Kan, T. Kondoh, S. Tagawa, Y. Yoshida: Proceedings of the Particle Accelerator Conference 2007.

Dynamic Optical Modulation of Electron Beam on a Photocathode RF Gun toward the Intensity Modulated Radiation Therapy (IMRT) (poster), \*T. Kondoh, H. Kashima, J. Yang, Y. Yoshida and S. Tagawa: The 7th International Symposium on Advanced Science Research ASR2007.

Reactions of solvated electrons in ionic liquid Diethylmethyl(2-methoxy)ammonium Bis(trifluoromethanesulfonyl)imide (poster), A. Asano, T. Kondoh, J. Yang, R. Nagaishi, K. Takahashi, Y. Yoshida: The 7th International Symposium on Advanced Science Research ASR2007.

Picosecond pulse radiolysis: dynamics of solvated electrons in ionic liquid and geminate ion recombination in liquid alkanes (poster), J. Yang, T. Kondoh, K. Norizawa, R. Nagaishi, M. Taguchi, K. Takahashi, R. Katoh, S. V. Anishchik, Y. Yoshida, and S. Tagawa: The 7th International Symposium on Advanced Science Research ASR2007.

Decomposition of halogenated organic chemicals in room temperature ionic liquids by ionizing radiation (poster), A. Kimura, M. Taguchi, T. Kondoh, J. Yang, Y. Yoshida, and H. Koichi: The 7th International Symposium on Advanced Science Research ASR2007.

Pulse Radiolysis Study of Water Effects on the Solvated Electrons in the Hydrophobic Liquid (poster), T. Kondoh, A. Asano, J. Yang, M. Taguchi, R. Nagaishi and Y. Yoshida: Proceedings of the 2nd International Congress on Ionic Liquids(COIL-2).

Pulse Radiolysis Study of Solvated Electrons Reactions in DEMMA-TFSI (poster), A. Asano, Ta. Kondoh J. Yang, R. Nagaishi K. Takahashi and Y. Yoshida: Proceedings of the 2nd International Congress on Ionic Liquids(COIL-2).

### **Contributions to International Conferences and Journals**

A. Yamaguchi Journal of Bacteriology (Editorial Board Member)

### **Publications in Domestic Meetings**

|                                                                                    |           |
|------------------------------------------------------------------------------------|-----------|
| 128 <sup>th</sup> The Pharmaceutical Society of Japan                              | 8 papers  |
| 81 <sup>th</sup> Japanese Society for Bacteriology                                 | 9 papers  |
| The 30 <sup>th</sup> Annual Meeting of the Molecular Biology Society of Japan, The | 12 papers |
| 80 <sup>th</sup> Annual Meeting of the Japanese Biochemical Society                |           |
| 29 <sup>th</sup> Membrane-Drug Interaction Symposium                               | 4 papers  |
| 33 <sup>th</sup> Japanese Bioenergetics Group                                      | 2 papers  |
| 19 <sup>th</sup> Symposium on Microbial Sciences                                   | 2 papers  |
| 4 <sup>th</sup> 21 <sup>st</sup> Century research conference on Escherichia coli   | 1 paper   |
| The 55 <sup>th</sup> Japanese Society of Chemotherapy                              | 2 papers  |
| Atomic Energy Society of Japan                                                     | 4 papers  |
| The Physical Society of Japan                                                      | 2 papers  |
| Japanese Society of Radiation Chemistry                                            | 8 papers  |
| Particle Accelerator Society of Japan                                              | 5 papers  |
| RF gun meeting                                                                     | 4 papers  |

### **Sponsorship**

#### **Grant-in-Aid for Scientific Research (S)**

|              |                                                                                    |             |
|--------------|------------------------------------------------------------------------------------|-------------|
| A. Yamaguchi | Structures, functions, regulations and physiological roles of xenobiotic exporters | ¥18,000,000 |
|--------------|------------------------------------------------------------------------------------|-------------|

#### **Grant-in-Aid for Scientific Research (A)**

|            |                                                                                                  |             |
|------------|--------------------------------------------------------------------------------------------------|-------------|
| Y. Yoshida | Research on Equivalent velocity spectroscopy for Sub-femtosecond and Attosecond Pulse Radiolysis | ¥13,130,000 |
|------------|--------------------------------------------------------------------------------------------------|-------------|

**Grant-in-Aid for Scientific Research (C)**

|          |                                                                |            |
|----------|----------------------------------------------------------------|------------|
| T. Nishi | Elucidation of the secretion mechanism of the lipid mediators. | ¥2,210,000 |
|----------|----------------------------------------------------------------|------------|

**Entrusted Research**

|              |                                                                                          |                                                                                                                                                       |             |
|--------------|------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| A. Yamaguchi | Japan Science and Technology Agency (CREST)                                              | Investigation of the Structure and Function for Xenobiotics Transporters and Clarification of Multidrug Resistance Mechanism                          | ¥3,023,000  |
| A. Yamaguchi | The Program of Founding Research Centers for Emerging and Reemerging Infectious Diseases | Exhaustive, systematic analysis of bacterial pathogenicity and transcriptional regulation of multidrug transporters, and new strategy for drug design | ¥300,000    |
| A. Yamaguchi | National Institute of Biomedical Innovation                                              | Development of novel inhibitors that counteract infectious diseases by drug resistant bacteria                                                        | ¥75,385,000 |

**Cooperative Research**

|            |                                             |                                                                                                |
|------------|---------------------------------------------|------------------------------------------------------------------------------------------------|
| Y. Yoshida | National Institute of Radiological Sciences | The research about the beam control for the particle beam cancer therapy.                      |
| Y. Yoshida | Sumitomo Heavy Industries, LTD              | Research on photocathode RF gun and high brightness electron beam.                             |
| Y. Yoshida | Japan Atomic Energy Agency Takasaki         | The research about the ion beam induced chemical reaction process by the ion pulse radiolysis. |
| Y. Yoshida | Japan Atomic Energy Agency Kansai           | Basic research for application of femtosecond electron beam driven by high intensity laser.    |

## Human Interface Research Group

Professor: Hiroshi KATAYAMA-YOSHIDA  
Masayuki NUMAO, Riichiro MIZOGUCHI

Specially Appointment Staff

Professor: Sunao TAKAFUJI  
Associate Professor: Takashi Kei SAITO  
Assistant Professor: Makoto NAKAZAWA, Ken-ichi FUKUI,

### Outline

Our research interests are building novel sensor and software systems, which enable analyzing human bio-signals, behaviors, and social information. Furthermore, we also perform econometrical researches on a new industrial prediction and strategically intellectual property accompanying from the information about industrial structure transitions.

### Current Research Projects

#### **Research on knowledge sharing technology for manufacturing support with safety, ease, and creation (Takafuji, Mizoguchi)**

- 1) We drastically improved OntoGear which is the software that supports engineers to externalize and utilize functional knowledge with added functionality such as integration model of failure knowledge and functional one.
- 2) Accomplishment of creating “Way Knowledge Editor”, which is other useful software, brings engineers in organizing and sharing way knowledge with combination use of OntoGear.
- 3) As several companies began with test use of OntoGear we had some support work for them to install that software. Moreover, we confirmed that OntoGear is available for the use of design support of fuel cell battery.

#### **Research on the strategic new industry prediction accompanying change of industrial structure (Katayama-Yoshida, Nakazawa)**

- 1) Under the commercial law of Japan, firms are classified into three groups according to capital: big, middle-sized and small companies. We showed that the growth rates of profit for the groups increased in the order of capital from small to big. The result indicates that capital can be an important index to discuss the growth dynamics of the firms.
- 2) We have developed an intellectual property map created by mapping both patent descriptions of interest and the keywords selected from the patent descriptions at the calculated position in the same plane, and implemented a beta version program to create the intellectual property map.

### **The adaptive interface by the sensor network and machine learning (Numao, Fukui)**

- 1) We have a system modeling affective-based music compositional intelligence. By investigating the use of emotion data derived from analyzing change in activity in the autonomic nervous system, we have speeded up its process ten times faster.
- 2) We are developing a reliability diagnosis support for a solid energy device. We have proposed an appropriate extraction method for Acoustic Emission waves and its sequential analysis method.

### **Research on cell manipulation device / platform robot for the research integration (Saito)**

- 1) We developed a novel integrated micro channel array for cell membrane perforation, cell membrane perforating nanorods, which are excellent terms of mass productivity and a large scale application and a robot microscope system to optimize of the perforation process.
- 2) We extended the application fields of the robot with self balancing function, and started a collaborative research to develop a commercial model of our unique long range manipulator.

## **Publications**

### **Original Papers**

Visualization Method for Fracture Dynamics in Solid Oxide Fuel Cell, Ken-ichi Fukui, Kazuhisa Sato, Junichiro Mizusaki, Kazumi Saito, Masayuki Numao: Information Technology Letters, 6 (2007) 5-8.

Evaluation of Vector Representative Topics that were Extracted Automatically, Ken-ichi Fukui, Kazumi Saito, Masahiro Kimura, Masayuki Numao: The Information Processing Society of Japan, Transactions on Mathematical Modeling and its Applications (IPSJ-TOM), 48 (SIG 6) (2007) 1-11.

### **Patents**

“DEVICE FOR SUPPORTING DOCUMENT UNDERSTANDING”, S. Takafuji, R. Mizoguchi, Y. Kitamura, 2007-158581.

“DOCUMENT PROCESSING DEVICE AND DOCUMENT PROCESSING METHOD”, S. Takafuji, Justsystems Corporation, PCT/JP2006/30162

“METHOD OF PERFORATING MEMBRANE AND APPARATUS THEREFORE”, Takashi Saito, United States Patent: 7,320,885

T. Saito, International patent application number: PCT/JP2007/066233

T. Saito, patent application number: 2008-039483



## **International Conferences**

Reliability Evaluation of SOFC under Simulated Operating Condition, \*Kazuhisa Sato, Norihiro Imanaka, Ken-ichi Fukui, Masayuki Numao, Shintaro Kyotani, Keiji Yashiro, Tatsuya Kawada, Toshiyuki Hashida, Junichiro Mizusaki: 10th International Symposium on Solid Oxide Fuel Cells (SOFC-X), Japan, Jun 2007.

Interpretable Likelihood for Vector Representable Topic, \*Ken-ichi Fukui, Kazumi Saito, Masahiro Kimura, Masayuki Numao: 11th International Conference on Knowledge-Based and Intelligent Information & Engineering Systems (KES), Italy, Sep 2007.

Combining Burst Extraction Method and Sequence-based SOM for Evaluation of Fracture Dynamics in Solid Oxide Fuel Cell, \*Ken-ichi Fukui, Kazumi Saito, Masahiro Kimura, Masayuki Numao: 19th IEEE International Conference on Tools with Artificial Intelligence (ICTAI), Greece, Oct 2007.

Evaluation of Fracture Dynamics in SOFC by Burst Extraction Method and Sequence-based SOM (poster), \*Ken-ichi Fukui, Kazuhisa Saito, Junichiro Mizusaki, Kazumi Saito, Masayuki Numao: 11th SANKEN and 6th Nanotechnology Center and 1st MSTEC International Symposium, Japan, Feb 2008.

Photodynamic Perforation of Cell Membrane on Micro Channel Array Toward Intra Cellular Technology (poster), \*K. Iso, T.K. Saito, H. Muguruma, H. Tabata, S. Konishi: 20<sup>th</sup> IEEE International Conference on Micro Electro Mechanical Systems (MEMS) 2007, Kobe, Japan, January 21-25, 2007.

TOWARDS A REFERENCE ONTOLOGY FOR FUNCTIONAL KNOWLEDGE INTEROPERABILITY, \*Yoshinobu Kitamura, Sunao Takafuji, Riichiro Mizoguchi: the ASME 2007 International Design Engineering Technical Conferences & Computers and Information in Engineering Conference, U.S.A., Sep 2007.

## **Publications in Domestic Meetings**

|                                                                 |          |
|-----------------------------------------------------------------|----------|
| Japanese Society of Artificial Intelligence                     | 1 paper  |
| The 21 <sup>st</sup> Annual Conference of JSAI                  | 1 paper  |
| Information Processing Society of Japan                         | 1 paper  |
| The Electrochemical Society of Japan                            | 1 paper  |
| The Japan Society of Applied Physics and Related Societies      | 2 paper  |
| The Life Science Research Network Symposium                     | 1 papers |
| Sensor Symposium on Sensors, Micromachines, and Applied Systems | 1 papers |
| Publications in The Physical Society of Japan                   | 1 paper  |
| Publications in Japan Society for Intellectual Production       | 1 papers |

## **Sponsorship**

### **Grant-in-Aid for Scientific Research on Exploratory Research**

|                            |                                                                                               |                                                                                                           |            |
|----------------------------|-----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|------------|
| T.K.Saito                  | Cell therapy system with cell membrane perforating nano rods                                  | ¥2,300,000                                                                                                |            |
| M. Nakazawa                | Research on the strategic new industry prediction accompanying change of industrial structure | ¥1,800,000                                                                                                |            |
| <b>Other Research Fund</b> |                                                                                               |                                                                                                           |            |
| S. Takafuji                | Justsystems Corporation                                                                       | Research on knowledge sharing by utilization of both ontology engineering and natural language processing | ¥6,500,000 |
| T.K. Saito                 | Atect Corporation                                                                             | Novel cell membrane perforation method for introduction of genes and drugs into cell                      | ¥3,200,000 |
| T.K. Saito                 | NIPPI Corporation                                                                             | Telescopic boom mechanism for spacecrafts                                                                 | ¥1,000,000 |

# Post-Silicon Materials and Devices Research Alliance

## Outline

“Post-Silicon Materials and Devices Research Alliance” was started to attempt strategic development of the post-silicon materials and devices as a cooperative research project with Institute of Multidisciplinary Research for Advanced Materials, Tohoku University in fiscal year 2006 and further with Research Institute for Electronic Science, Hokkaido University and Chemical Resources Laboratory, Tokyo Institute of Technology in fiscal year 2007. This alliance consists of three research groups; Molecular Nano-Electronics research group, New Functional Nano-Electronics research group and Molecular Nano-Mechanics & Bio-Mechanics research group

This Post-Silicon Alliance is being run under the Steering Committee of 4 member Institutes. The Committee members from ISIR are Prof. H. Asahi (Chair), Prof. T. Kawai, Prof. Y. Hirotsu, and Prof. Y. Aso. The members of this Post-Silicon Alliance from ISIR are as follows.

(1) Molecular Nano-Electronics Research Group)

Prof. Y. Aso (Group Leader), Prof. H. Iwasaki (Group Sub-Leader), Prof. T. Kawai, Prof. S. Tagawa

(2) New Functional Nano-Electronics Research Group)

Prof. Y. Hirotsu (Group Leader), Prof. K. Matsumoto (Group Sub-Leader), Prof. H. Asahi, Prof. K. Tanimura, Prof. H. Kobayashi

(3) Molecular Nano-Mechanics & Bio-Mechanics Research Group)

Prof. N. Kato (Group Leader), Prof. H. Noji (Group Sub-Leader), Prof. K. Nakatani

## Achievements

- Development of functionalized molecular wires and n-type organic semiconductors
- Understanding of STM light emission and SPM observation of nanostructure dynamics
- Elucidation of charge carrier dynamics in single crystal of organic semiconductor
- Single molecule conductance measurement and surface potential imaging on insulating substrates
- Coherent transport and Coulomb blockade transport in carbon nanotube device
- Enhancement of magnetization of GaGdN and fabrication of GaCrN nano-rods
- Formation of a novel  $sp^3$ -bonded phase of carbon from graphite by fs-laser excitation
- Formation processes of iron silicide nanoparticles studied by *in situ* TEM
- Development of SiC oxidation at 120°C and achievement of good MOS characteristics
- Synthesis of bivalent GGTase-I inhibitors targeting interior and exterior protein surfaces
- Single-molecule analysis of a novel reaction intermediate of a rotary molecular motor, F1-ATPase
- Realization of photoresponsive molecular glue of DNA

# Molecular Nano-Electronics Research Group

Professor: Yoshio ASO (Group Leader), Hiroshi IWASAKI (Group Sub-Leader)  
Seiichi TAGAWA, Tomoji KAWAI

## Outline

We have been focusing our research on the design, synthesis, and properties of (1) novel extended conjugation systems as active materials for organic electronic and photoelectronic devices and (2) nano-scale conjugated molecules for promising functional molecular wires.

For post silicon technologies, it is important to prepare various kinds of substrates with atomically flat surfaces, to make nano-structures on those surfaces, and to use organic materials and biomaterials as components of devices. It is required to develop analysis and characterization methods of the mesoscopic structures and their physical and electronic properties. We study, by using scanning tunneling microscope (STM) and atomic force microscope, (1) preparation of atomically flat surfaces of various substrates such as  $\text{SrTiO}_3$  and Si and nanofabrication on these surfaces, (2) protein crystal growth and (3) STM-light emission of organic films. The last subject is studied together with Misawa laboratory at Hokkaido university and Aso laboratory in our institute.

Using time-resolved microwave conductivity (TRMC) which enables us to measure nano-scale electric conductivity in organic semiconductors, we elucidated the optoelectronic properties, i.e. photoconductivity in organic single crystals such as rubrene and annulene.

As the research of molecular-scale devices based on the function of single molecule, we are developing new techniques for the measurement of electrical properties for molecular nanostructures. We are also developing an interconnect method to program three kinds of component molecules with their own functions, and to create a molecular device between nano-scale electrodes in a self-organized manner.

## Current Research Projects

### Organic Electronics Materials

We have developed. We have designed fluorine- and/or carbonyl-functionalized cyclopentene-annelated aromatic units synthesized their based conjugated oligomers as organic materials for n-type field-effect transistors. Some of these electronegative oligomers revealed high field-effect electron mobility.

### Molecular Electronics Materials

The cyclopentathiophene monomer units with bulky t-butyl diphenylsilyl groups or with a spiro-type substituted dioctylfluorene have been designed, and then a series of their oligomers up to 12-mer were synthesized as insulated molecular wires. The electronic absorption spectra of oxidized species of these insulated oligothiophenes showed complete blocking of pi-dimer formations unlike usual oligothiophenes.

It is highly important to connect each molecular wire to the bulk nano-gap electrode. We have achieved the synthesis of the thiophene 24-mers with terminal thiol anchor groups for gold electrodes as well as with terminal ethynyl anchor groups for silicon electrodes and succeeded in conduction measurement of the thiol-anchor molecular wire

by use of a nano-gap gold electrode.

For certain connection of molecular wires with metal electrodes and efficient carrier injection, we have developed tetraphenylmethane tripodal anchor units with various functional groups and found unique adsorption properties of the selenium anchors on a gold electrode.

### **Formation of nanostructures on atomically flat substrates**

Understanding of the stability of nanoscale structures on crystal surfaces is significant for development of nanoscale devices. Performing real-time observation of thermal relaxation of multilayer holes on SrTiO<sub>3</sub>(001) surfaces, decay dynamics for the system where short range step-step interactions exist has been clarified.

### **Mechanism of Protein Crystallization**

A variety of chemical compounds have proven useful in promoting protein crystallization, however, the understanding of the role of specific ions in the intermolecular interactions in aqueous solution remains elusive. In this work, the ion specific effect of Na<sup>+</sup> and K<sup>+</sup> ions on intermolecular interactions between thaumatin molecules has been studied. It has been found that such monovalent cations affect the molecular arrangement of the tetragonal thaumatin crystals, interacting with the specific residues of thaumatin molecules.

### **STM-light emission of organic films**

We investigate scanning tunneling microscope (STM)-excited fluorescence from porphyrin thin films on various combinations of substrates (Pt, Ag, Au and ITO) and PtIr, Ag and Au tips. We calculate relative electromagnetic-field powers in the tip-substrate gaps, which are in consistent with the observed intensities of the plasmon-mediated light emissions. We find enhancement of STM-excited fluorescence owing to field confinement effect and plasmonic gap modes.

### **Charge carrier dynamics in single crystal rubrene**

We reported charge carrier dynamics in single-crystal rubrene studied by time-resolved microwave conductivity and transient photoabsorption/emission spectroscopies upon exposure to 355 nm. Based on the comparison of the kinetics and extinction coefficients of radical cation/anion estimated by pulse radiolysis, the minimum alternating-current mobility of  $(5.2 \pm 0.7) \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  was obtained without electrodes and resolved into hole and electron components, i.e. exhibition of ambipolar nature. The dynamics and optoelectronic property are discussed in terms of second-order reaction, exciton-exciton annihilation, quantum efficiency, triplet contribution, and density functional theory. Anisotropic mobility is also measured by utilizing defined direction of microwave electric field, suggesting the band-like motion on the nanometer-scale conduction. Time-resolved conductivity and photoabsorption studies of single-crystal rubrene provide important information on the intrinsic nature of charge carrier transport.

### **Development of nanofabricated mechanically controllable break junction**

The outstanding mechanical stability of the nano-fabricated mechanically controllable break junction establishes an ideal experimental platform to study electron transport in single molecules by realizing unprecedented long-time holding of single molecule junctions, about 10000 times more potent than the conventional techniques such as

SPM break junctions.

#### **Metallic nature of metal-molecule interface formed by Au-Se bonds**

We determined the structure and electronic states of the metal-molecule interface formed by Au-Se bonds, and found that the interface is a useful metal-molecule interface from the viewpoint of molecular devices. These results indicate that metal-molecule interfaces formed by Au-Se bonds have high potential for improving the properties of molecular devices that are currently being developed, such as organic field-effect transistors, organic electroluminescence devices, biochips, and nanoscale molecular devices.

#### **Surface potential and capacitance image of biological molecules on *insulating* substrates**

We found that potential and capacitance images of nanoscale adsorbates on *insulating* substrates can be obtained by frequency-mode surface potential microscopy. This finding is beyond the common understanding based on parallel-plate condenser model because the field modulation between tip and insulator surface should be too small to probe the surface potential variation, and the charges of surface adsorbates should be almost negligible in comparison with that of bulk substrate. However, the assumption of these consideration collapsed because the external electric field just below a sharp tip apex was enough strong to modulate tip-adsorbates electrostatic interactions. We are conducting systematic analysis for electrostatic force imaging on insulating substrate.

#### **Anchoring Gold Nanoparticles onto a Mica Surface by Oxygen Plasma Ashing for Sequential Nanocomponent Assembly.**

Water-soluble gold nanoparticles can be immobilized in both polar (water) and nonpolar liquid (chloroform) on hydrophilic mica surface by oxygen plasma ashing. It was demonstrated that a DNA with a thiol at an extremity is attached to the immobilized nanoparticles due to the gold-thiol coupling, and stretched in the flow direction of the following water rinse. This technique allows a sequential integration of nanoparticles and molecules for various solutions, since the nanoparticles remains on a solid surface rather than dissolve into the solution. The technique is being used for bottom-up construction of molecular nanostructures.

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#### **Contributions to International Conferences and Journals**

Y. Aso                      12th International Symposium on Novel Aromatic Compounds  
                                  (Organizing Committee, Financial Chair)

H. Iwasaki                Scanning Probe Microscopy, Sensors and Nanostructures June 3-  
                                  6, 2006, Palais des Congrès, La Grande Motte, France  
                                  (Committee member)

#### **Publications in Domestic Meetings**

|                                            |           |
|--------------------------------------------|-----------|
| The Chemical Society of Japan              | 7 papers  |
| Symposium on Main Element Chemistry        | 1 paper   |
| Symposium on Organic pi-Systems            | 2 papers  |
| Symposium on Structural Organic Chemistry  | 3 papers  |
| The Chemical Society of Japan/Kanto Branch | 1 paper   |
| The Society of Polymer Science, Japan      | 1 paper   |
| The Japan Society of Radiation Chemistry   | 2 papers  |
| The Japan Society of Applied Physics:      | 19 papers |

|                                     |          |
|-------------------------------------|----------|
| The Japan Society of Polymer        | 2 papers |
| The Physical Society of Japan       | 7 papers |
| Japan Society for Molecular Science | 3 papers |
| Others                              | 6 papers |

## **New Functional Nano-Electronics Research Group**

Professors: Yoshihiko HIROTSU (Group Leader),  
Kazuhiko MATSUMOTO (Group Sub-Leader),  
Hajime ASAH, Katsumi TANIMURA, Hikaru KOBAYASHI

### **Outline**

New functional nano-electronics research group treated mainly the semiconductor and its material characteristics, physical evaluation, device performance, etc. are analyzed in details as follows:

The Synthesis and development of III-nitride semiconductor-based room temperature transparent ferromagnetic semiconductors with strong photoemission properties and their application to novel semiconductor nano-spintronics device fabrications are conducted. (Asahi)

By modifying the CNT electrodes with enzyme glucose oxidase, glucose molecules could be detected using our chips by cyclic voltammetry and chronoamperometry. We conclude that microfluidic chips with CNT-arrayed electrodes are a promising candidate for the development of hand-held electrochemical biosensors. (Matsumoto)

The aim of our research is to establish the new methods to fabricate highly functional nano-electronic materials and structures by controlling modes of condensation via electronic excitation of solids. (Tanimura)

Using the in situ TEM observations indicated that an amorphous Fe-Si layer was formed on the Si substrate in the as-deposited specimen. This amorphous layer was crystallized into epsilon-FeSi after thermal annealing, and then hemispherical epsilon-FeSi particles together with metastable gamma-FeSi<sub>2</sub> were formed just beneath the surface of the Si substrate. (Hirotsu)

SiO<sub>2</sub>/SiC structure has been fabricated by use of two-step nitric acid oxidation method in which low concentration nitric acid and azeotropic nitric acid aqueous solutions are employed. Although the leakage current density of the fabricated MOS diodes was high, it greatly decreased by performing hydrogen treatment at 400°C before nitric acid oxidation. (Kobayashi)

### **Current Research Projects**

#### **Low Temperature Growth of III-Nitride-Based Magnetic Semiconductors**

Transition-metal and rare-earth doped GaN magnetic semiconductors are gathering great interest as new functional materials to fabricate semiconductor spintronics devices because of their ferromagnetic properties and strong photo emission properties at room temperature. We have grown Gd-doped GaN layers at low growth temperatures and observed the increased incorporation of Gd atoms and the enhancement of magnetization. By the co-doping of Si atoms, further enhancement of magnetization was realized.

#### **Growth of GaCrN Nano-Rods**

To fabricate magnetic semiconductor nano-devices, we have investigated the formation of GaCrN nano-rod structures. GaCrN nano-rods were grown on n-Si (100) substrates with native oxide layer. It was found that the GaCrN nano-rods without segregation of

CrN were formed by the growth of lowered substrate temperatures (550°C). The grown GaCrN nano-rods exhibited room temperature ferromagnetism.

#### **Fabrication of amperometric biosensors based on carbon nanotube-arrayed electrodes**

We fabricated carbon nanotube (CNT) amperometric chips with pneumatic micropumps by the combination of amperometric biosensors based on CNT-arrayed electrodes and microchannels with pneumatic micropumps. By modifying the CNT electrodes with enzyme glucose oxidase, glucose molecules could be detected using our chips by cyclic voltammetry and chronoamperometry. We conclude that microfluidic chips with CNT-arrayed electrodes are a promising candidate for the development of hand-held electrochemical biosensors.

#### **Mechanism of Low-Energy Electron Interaction with Semiconductor Surfaces**

Local structural changes induced by typically 10-eV electron irradiation on hydrogen-terminated Si(001)-(2x1) and Si(111)-(7x7) surfaces have been studied by means of scanning tunnelling microscopy. Inelastic excitation from bonding- to antibonding states of S-H bond is responsible for the bond rupture of Si-H bonds. On the other hand, Inelastic Plasmon excitation induces local bond rupture on Si(111)-(7x7).

#### **Preferential P-atomic Removal on InP(110)-(1x1) by Tunnelling Hole Injection from STM Tip.**

Injection of holes into valence band from STM tips at a bias of a few eV induces preferential anion surface atoms from III-V semiconductor surfaces. Direct patterning at atomic levels is thus possible by this unique surface-structural modification.

#### **Graphite-to-Diamond Phase Transition Induced by Femtosecond-Laser excitation**

Femtosecond laser excitation induced structural phase transformation from Graphite to sp<sup>3</sup>-bonded new phase of carbons on Graphite surfaces. STM observation has revealed precursor configurations with local inter-layer bonded structures.

#### **Formation processes of iron silicide nanoparticles**

The formation processes of iron silicide nanoparticles dependent on thermal annealing were examined by *in situ* transmission electron microscopy (TEM). An Fe thin film with a thickness of ~2 nm was deposited on a Si(100) substrate at room temperature using an electron-beam evaporation method, followed by thermal annealing at temperatures ranging from 573 K to 1173 K. *In situ* TEM observations indicated that an amorphous Fe-Si layer was formed on the Si substrate in the as-deposited specimen. This amorphous layer was crystallized into *epsilon*-FeSi after thermal annealing, and then hemispherical *epsilon*-FeSi particles together with metastable *gamma*-FeSi<sub>2</sub> were formed just beneath the surface of the Si substrate. With increasing annealing temperature, the *epsilon*-phase changed to hemispherical *gamma*-FeSi<sub>2</sub> nanoparticles, and finally the *gamma*-FeSi<sub>2</sub> particles transformed into pyramidal *beta*-FeSi<sub>2</sub> particles.

#### **Low temperature fabrication of SiC-MOS devices by use of nitric acid oxidation method**

SiO<sub>2</sub>/SiC structure has been fabricated by use of two-step nitric acid oxidation method in which low concentration nitric acid and azeotropic nitric acid aqueous solutions are employed. Although the leakage current density of the fabricated MOS diodes was high, it greatly decreased by performing hydrogen treatment at 400°C before nitric acid oxidation. The decrease in the leakage current density by the hydrogen treatment is attributed to i) Smoothing of the SiO<sub>2</sub>/SiC interfaces, ii) Removal of SiO<sub>2</sub> gap-states, and iii) increase in the energy barrier height at the SiO<sub>2</sub>/SiC interfaces.

### **Development of cleaning technology for SiC**

We have found that metal contaminants on SiC cannot be completely removed by the conventional RCA method, but can by use of the RCA method and HCN cleaning method.

## **Publications**

### **Original Papers**

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Properties of thick SiO<sub>2</sub>/Si structure formed at 120°C by use of two-step nitric acid oxidation method, S. Imai, S. Mizushima, Asuha, W.-B. Kim, and H. Kobayashi, *Appl. Surf. Sci.* 254, 3685-3689 (2008).

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### **Review Papers**

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Local Structure and Crystallization Process of Amorphous Fe-Si Thin Layers, M. Naito, A. Hirata, M. Ishimaru, and Y. Hirotsu, *J. Cryst. Soc. Jpn.* 49 (2007) 115-121 (in Japanese).

Electron Diffraction Structure Analysis of Phase-Change Recording Materials, M. Naito, M. Ishimaru, and Y. Hirotsu, *Materia Japan* 46 (2007) 652-659 (in Japanese).

### **Books**

## **Patents**

Semiconductor devices and method of fabrication of semiconductor devices, H. Nagasawa, N. Hatta, T. Kawahara, and H. Kobayashi, Tokugan 2007-293258.

Formation method of insulating layers, apparatus for insulating layer formation, production method of semiconductor apparatuses, semiconductor apparatuses, and method of surface treatment of silicon carbide substrates, H. Kobayashi, PCT/JP2007/64759.

## **International Conferences**

MBE Growth and Characterization of Rare-Earth Doped Nitride Semiconductors for Spintronics (INVITED), H. Asahi, Y.K. Zhou, S. Emura and S. Hasegawa, E-MRS2007, Strasbourg, France, May 28- June 1, 2007.

High Gd concentration GaGdN grown at low temperature, Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi, SpinTech-IV, Hawaii, USA, June 20-22, 2007.

Enhancement of magnetic moment in GaGdN/GaN superlattice structure, Y.K. Zhou, S.W. Choi, S. Kimura, S. Emura, S. Hasegawa and H. Asahi, Material Today Asia, Loong Palace Hotel, Beijing, China, September 3-5, 2007.

Growth and characterization of InCrN and (In,Ga,Cr)N diluted magnetic semiconductors, S. Kimura, S. Emura, Y. Hiromura, Y.K. Zhou, S. Hasegawa and H. Asahi, 7th International Conference on Nitride Semiconductors, Las Vegas, Nevada, USA, September 16-21, 2007.

High-sensitive Label-free Biosensors Based on Carbon Nanotube Field-effect Transistors Modified with Aptamer, K. Maehashi, T. Katsura, K. Matsumoto, K. Kerman, Y. Takamura and E. Tamiya, *NSTI Nanotech 2007* (2007) May 20-24, Santa Clara, USA

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Improvement of Hysteresis Characteristics in Carbon Nanotube Field-Effect Transistor, K. Nishiguchi, Y. Ohno, K. Maehashi, K. Inoue, and K. Matsumoto, The 34th International Symposium on Compound Semiconductors, (2007) Oct. 15-18, Kyoto, Japan

Laser-Irradiated Chemical Vapor Deposition for Growth of Single-Walled Carbon Nanotube, Y. Asai, Y. Fujiwara, K. Maehashi, Y. Ohno, K. Inoue, and K. Matsumoto, The 34th International Symposium on Compound Semiconductors, (2007) Oct. 15-18,

Kyoto, Japan

Excitation-induced atomic desorption and structural instability of semiconductor surfaces (INVITED), K. Tanimura, 11<sup>th</sup> international workshop on “Desorption Induced by Electronic Transitions, March 11-15, 2007, Berlin, Germany

Excitation-wavelength dependent ultrafast carrier dynamics on Si surfaces, T. Ichibayashi, S. Tanaka, and K. Tanimura, 11<sup>th</sup> international workshop on “Desorption Induced by Electronic Transitions”, March 11-15, 2007, Berlin, Germany

Hydrogen removal from Si(001)-2x1:H surface induced by low-energy electron beam excitation, K. Ichihashi, J. Kanasaki, and K. Tanimura, 11<sup>th</sup> international workshop on “Desorption Induced by Electronic Transitions”, March 11-15, 2007, Berlin, Germany

In situ TEM study on the formation process of iron silicide nanoparticles on Si substrate, J. H. Won, A. Kovacs, M. Ishimaru, Y. Hirotsu, Materials Research Society 1998 Fall Meeting, Boston, USA (2007.11)

Fabrication of Oriented Hard-Magnetic Alloy Nanoparticles and Their Characterization, Y. Hirotsu, K. Sato, A. Kovacs, H. Naganuma, H.W. Ryu, 1st International Symposium on Advanced Magnetic Materials, Sendai (2008.1).

Nitric Acid Oxidation of Si and SiC for the Low Temperature Fabrication of MOS Structure, H. Kobayashi, Asuha, T. Matsumoto and M. Takahashi, International Seminar on Semiconductor Surface Passivation 2007.

Surface Chemistry in Si Cleaning with Cyanides Solutions, M. Takahashi, Y.-L. Liu and H. Kobayashi, International Seminar on Semiconductor Surface Passivation 2007.

Photoluminescence of Passivated a-Si:H, R. Btunner, E. Pincik, H. Kobayashi, M. Takahashi, M. Kucera and J. Rusnak, International Seminar on Semiconductor Surface Passivation 2007.

Nitric Acid Oxidation of Si (NAOS) and Defect Passivation Etch-Less Cleaning (DPEL) Methods to Improve Si Device Characteristics, T. Matsumoto, Asuha, Y.-L. Liu, S. Imai, S. Mizushima, M. Takahashi and H. Kobayashi, 3rd Handai Nano Symposium.

Nitric Acid Oxidation of SiC for Fabrication of 3C-SiC Based MOS Devices, H. Kobayashi, S. Im, M. Takahashi and H. Nagasawa, International Conference on Silicon Carbide and Related Materials 2007.

Removal of Copper Adsorbate from Silicon Surfaces by the use of Semiconductor Cleaning Solutions with Capability of Defect Passivation, M. Takahashi, H. Narita, T. Shishido, H. Iwasa and H. Kobayashi, 11th Sanken, 6th Nanotechnology Center and 1st MSTEC International Symposium.

### **Contributions to International Conferences and Journals**

|              |                                                                                                                                   |
|--------------|-----------------------------------------------------------------------------------------------------------------------------------|
| H. Asahi     | 15th International Conference on Molecular Beam Epitaxy<br>(International Advisory Committee member)                              |
| H. Asahi     | International Symposium on Compound Semiconductors 2007<br>(Organizing Committee member, Program Committee member)                |
| H. Asahi     | Journal of Crystal Growth (Editor)                                                                                                |
| H. Asahi     | J. Materials Science: Materials in Electronics (Editorial Board member)                                                           |
| K. Matsumoto | International Conference on Solid State Device & Materials 2007(Program Sub-Committee Chair)                                      |
| K. Matsumoto | International Conference on Compound Semiconductor 2007(Program Committee member)                                                 |
| K. Matsumoto | International Symposium on Nanotechnology(Organizing Committee member)                                                            |
| K. Matsumoto | IEEE Nanotechnology (Associate Editor)                                                                                            |
| K. Matsumoto | Japanese Journal of Applied Physics (Editor, STAP 7 Special Editor-in-Chief)                                                      |
| K. Tanimura  | 11 <sup>th</sup> international workshop on Desorption Induced by Electronic Transitions (International Steering Committee member) |
| Y. Hirotsu   | 7 <sup>th</sup> Polish-Japanese Joint Seminar on Micro and Nano Analysis (Advisory Committee)                                     |
| H. Kobayashi | Applied Surface Science (Editor-in-Chief)                                                                                         |
| H. Kobayashi | Vth International Workshop on Semiconductor Surface Passivation (International Scientific Committee)                              |
| H. Kobayashi | 4 <sup>th</sup> Vacuum and Surface Science Conference of Asia and Australia (Publishing Committee)                                |

### **Publications in Domestic Meetings**

|                                                                 |           |
|-----------------------------------------------------------------|-----------|
| The Japan Society of Applied Physics                            | 9 papers  |
| PASPS Symposium                                                 | 5 papers  |
| Electronic Materials Symposium                                  | 1 paper   |
| International Conference on Solid State Device & Materials 2007 | 2 papers  |
| The Japan Physical Society                                      | 12 papers |
| The Japan Institute of Metals                                   | 7 papers  |
| The Japanese Society of Microscopy                              | 4 papers  |
| The Surface Science Society of Japan                            | 2 papers  |
| Surface and Interface Spectroscopy                              | 1 paper   |

### **Sponsorships**

#### **Grant-in-Aid for Specially Promoted Research**

|             |                                                     |              |
|-------------|-----------------------------------------------------|--------------|
| K. Tanimura | Dynamical studies of photoinduced phase transitions | ¥188,110,000 |
|-------------|-----------------------------------------------------|--------------|

**Grant-in-Aid for Scientific Research on Priority Areas**

|            |                                                                                           |            |
|------------|-------------------------------------------------------------------------------------------|------------|
| H. Asahi   | Study on Fabrication of InN-Based Long Wavelength Circular Polarized Semiconductor Lasers | ¥3,700,000 |
| Y. Hirotsu | In situ observation of atomistic structures in metallic liquid and metallic glass         | ¥9,800,000 |

**Grant-in-Aid for Scientific Research (S)**

|            |                                                                                                   |             |
|------------|---------------------------------------------------------------------------------------------------|-------------|
| Y. Hirotsu | Fabrication and characterization of hard magnetic alloy nanoparticles produced by vapor quenching | ¥14,430,000 |
|------------|---------------------------------------------------------------------------------------------------|-------------|

**Grant-in-Aid for Scientific Research (A)**

|             |                                                                                      |            |
|-------------|--------------------------------------------------------------------------------------|------------|
| K. Tanimura | Dynamical properties of excited semiconductor surfaces with two-dimensional features | ¥2,300,000 |
|-------------|--------------------------------------------------------------------------------------|------------|

**Grant-in-Aid for Scientific Research (B)**

|          |                                                                                                                         |            |
|----------|-------------------------------------------------------------------------------------------------------------------------|------------|
| H. Asahi | Study on Room Temperature Ferromagnetic Nitride Semiconductor Nanostructures and Application to Nanospintronics Devices | ¥5,500,000 |
|----------|-------------------------------------------------------------------------------------------------------------------------|------------|

**Grant-in-Aid for Exploratory Research**

|             |                                                                                         |            |
|-------------|-----------------------------------------------------------------------------------------|------------|
| K. Tanimura | Graphite-to-Diamond Structural Phase transformation Induced by visible-light excitation | ¥1,500,000 |
|-------------|-----------------------------------------------------------------------------------------|------------|

**Grant-in-Aid for Creative Scientific Research**

|          |                                                                                                     |             |
|----------|-----------------------------------------------------------------------------------------------------|-------------|
| H. Asahi | Development of properties and functionalities by precise control of rare-earth doping (Y. Fujiwara) | ¥30,420,000 |
|----------|-----------------------------------------------------------------------------------------------------|-------------|

**Entrusted Research**

|              |                                                                                  |                                                                                                             |             |
|--------------|----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|-------------|
| K. Matsumoto | Japan Science and Technology Organization                                        | Carbon nanotube single electron electron single spin measurement systems                                    | ¥65,000,000 |
| K. Matsumoto | New Energy & Industrial Technology Development Organization                      | Development of CNT High Sensitive Biosensor for Personal QOL System                                         | ¥18,000,000 |
| Y. Hirotsu   | NEDO (Advanced Materials Technology Utilizing Glassy Metals for Commercial Uses) | Nano-structure Analysis for the Evaluation of Mechanical Properties in Glassy Metals                        | ¥3,150,000  |
| Y. Hirotsu   | Matsushita Electric Works, Ltd.                                                  | Structure Characterization of Inorganic and Organic Materials on Glass Substrates                           | ¥400,000    |
| H. Kobayashi | Japan Science and Technology Organization                                        | Low temperature formation of TFT gate oxide layers and lower power consumption by the nitric acid oxidation | ¥53,469,022 |

|              |                                                 |                           |                |            |
|--------------|-------------------------------------------------|---------------------------|----------------|------------|
| H. Kobayashi | Japan Science and<br>Technology<br>Organization | Japan-Slovakia<br>project | joint research | ¥2,458,683 |
|--------------|-------------------------------------------------|---------------------------|----------------|------------|

## **Molecular Nano-Mechanics & Bio-Mechanics Research Group**

Professors: Nobuo KATO (Group Leader), Hiroyuki NOJI (Group Sub-Leader)  
Kazuhiko NAKATANI

### **Outline**

With biomechanics of molecular motors, DNA, and other related materials, researches of this group aim at the development of devices functioning with self-organization on the basis of producing new material, nano light processing, nano measurement of extremely weak force, dynamic assessments of nano space. Kato group focused the attention on the photoresponsive gene expression with peptide nucleic acid and modulation of cell signaling by diterpenoid-based or peptide-mimetic type of small molecules. Noji group, in cooperation with the Nagai group of Research Institute for Electronic Science, Hokkaido University and Yoshida group of Chemical Resources Laboratory, Tokyo Institute of Technology, pushed forward a study about elucidation of the energy conversion mechanism of the ATP synthase with single molecule measurement technology and microdevices. Furthermore, they developed a fluorescent probe for ATP and measured dynamics of the ATP density in the cell. Nakatani group studied the photoresponsive molecular glue for DNA and realized the light control of the DNA double strand formation with photoswitchable molecular glue.

### **Current Research Projects**

#### **Synthesis of Bivalent GGTase-I Inhibitors Targeting Interior and Exterior Protein Surfaces**

As an attempt to improve binding selectivity of the organic agents to targeting protein surface, a series of bivalent enzyme inhibitors consisting two distinct modules, which were designed for complementary recognition of characteristic protein interior and exterior surfaces of mammalian Type-I geranylgeranyltransferase, was synthesized. The bivalent compounds showed submicromolar inhibition activity with the selectivity for GGTase-I over FTase in more than 150 times, demonstrating that our anchoring strategy to target protein exterior surface does not compromise the selectivity.

#### **Intracellular ATP Imaging**

With the aim of direct measurement of the intracellular [ATP] in individual cells, we have developed a ratiometric fluorescent ATP sensor protein. The ATP sensor protein was successively expressed in a culture cells such as a human cultured cell and bacteria cells. When apoptosis was induced in human cells, a large decrement in intracellular [ATP] level was reproducibly observed several seconds before the morphologic change of cell, which is characteristic of apoptosis, indicating the intracellular [ATP] drop is a trigger of apoptosis. This project has been done under the frame of the collaboration with Nagai lab in Hokkaido University.

#### **Single-molecule Study on a Rotary Molecular Motor Protein**

F<sub>1</sub>-ATPase is a rotary molecular motor that makes 120° stepping rotation, each step driven by a single ATP hydrolysis reaction. Since the establishment of the single-molecule rotation assay, attempts have been made to resolve the rotary motion of F<sub>1</sub>-

ATPase into discrete steps of ATP hydrolysis in order to clarify how the rotation is coupled with the elementary reaction steps of ATP hydrolysis. In the collaboration work with Yoshida lab in Tokyo Institute of Technology, we have found a new reaction intermediate of  $F_1$ -ATPase in the rotation assay at 4°C. Kinetic analysis shows that the intermediate state is relevant to ADP-releasing step.

### **Photoswitchable Molecular Glue**

We have developed molecular glue that adheres two single stranded DNA that does not spontaneously hybridize with each other. To incorporate the function of switching the molecular glue activity, photoswitchable molecular glue possessing the azobenzene chromophore that undergoes cis to trans photoisomerization was developed.

## **Publications**

### **Original Papers**

Fusicoccins are biosynthesized by an unusual chimeric diterpene synthase in fungi, T. Toyomasu, M. Tsukahara, A. Kaneko, R. Niida, W. Mitsunashi, T. Daiiri, N. Kato, and T. Sassa, *Proc. Nat. Acad. Sci. USA*. 104 (2007) 3084-3088.

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Visualization of RecA filaments and DNA by fluorescence microscopy, T. Nishinaka, Y. Doi, M. Hashimoto, R. Hara, T. Shibata, Y. Harada, K. Kinoshita Jr., H. Noji, and E. Yashima, *J. Biochem.* 141 (2007) 147-156.

Single molecule energetics of  $F_1$ -ATPase motor, E. Muneyuki, T. Watanabe-Nakayama, T. Suzuki, M. Yoshida, T. Nishizaka, and H. Noji, *Biophys. J.* 92 (2007) 1806-1812.

Coupling of Rotation and Catalysis in  $F_1$ -ATPase Revealed by Single-Molecule Imaging and Manipulation, K. Adachi, K. Oiwa, T. Nishizaka, S. Furuie, H. Noji, H. Itoh, M. Yoshida, and K. Kinoshita Jr., *Cell* 130 (2007) 309-321.

Thermally responsive supramolecular nanomeshes for on/off switching of the rotary motion of  $F_1$ -ATPase at the single-molecule level, S. Yamaguchi, S. Matsumoto, K. Ishizuka, Y. Iko, K.V. Tabata, H.F. Arata, H. Fujita, H. Noji, and I. Hamachi, *Chemistry* 14 (2007) 1891-1896.

An integrated system for enzymatic cleavage and electrostretching of freely-suspended single DNA molecules, L. Lam, S. Sakakihara, K. Ishizuka, S. Takeuchi, and H. Noji, *Lab on a Chip* 7 (2007) 1738-1745.

Temperature-sensitive reaction intermediate of  $F_1$ -ATPase, R. Watanabe, R. Iino, K. Shimabukuro, M. Yoshida, and H. Noji, *EMBO Reports* 9 (2008) 84-90.

Lipid bilayer microarray for parallel recording of transmembrane ion currents, B. Le



Pioufle, H. Suzuki, K.V. Tabata, and H. Noji, and S. Takeuchi, *Anal. Chem.* 80 (2008) 328-332.

Detection of L-DNA-Tagged PCR Products by Surface Plasmon Resonance Imaging, G. Hayashi, M. Hagihara, A. Kobori, and K. Nakatani, *ChemBioChem.* 8 (2007) 169-171.

Bidirectional control of gold nanoparticle assembly by turning on and off DNA hybridization with thermally degradable molecular glue, T. Peng, C. Dohno, and K. Nakatani, *ChemBioChem*, 8 (2007) 483-485.

Small-Molecule Binding to the Nonquadruplex Form of the Human Telomeric Sequence, Y. Goto, S. Hagihara, M. Hagihara, and K. Nakatani, *ChemBioChem.* 8 (2007) 723-726.

Allele Specific C-Bulge Probes with One Unique Fluorescent Molecule Discriminate the Single Nucleotide Polymorphism in DNA, F. Takei, H. Suda, M. Hagihara, J. Zhang, A. Kobori, and K. Nakatani, *Chem. Eur. J.* 13 (2007) 4452-4457.

Exploiting small molecule binding to DNA for the detection of single-nucleotide mismatches and their base environment, X. Li, H. Song, K. Nakatani, and H.-B. Kraatz, *Anal. Chem.* 79 (2007) 2552-2555.

The rare crystallographic structure of d(CGCGCG)(2): the natural spermidine molecule bound to the minor groove of left-handed Z-DNA d(CGCGCG)(2) at 10 °C, H. Ohishi, Y. Tozuka, Z. Da-Yang, T. Ishida, and K. Nakatani, *Biochem. Biophys. Res. Commun.* 358 (2007) 24-28.

Analysis of mismatched DNA by mismatch binding ligand (MBL)-Sepharose affinity chromatography, Y. Goto, H. Suda, A. Kobori, and K. Nakatani, *Anal. Bioanal. Chem.* 388 (2007) 1165-1173.

Emission of characteristic fluorescence from the ligand-cytosine complex in U<sub>A</sub>/ACU bulged RNA duplex, J. Zhang, F. Takei, and K. Nakatani, *Bioorg. Med. Chem.* 15 (2007) 4813-4817.

Photoregulation of a Peptide-RNA Interaction on a Gold Surface, G. Hayashi, M. Hagihara, C. Dohno, S. Uno, and K. Nakatani, *J. Am. Chem. Soc.* 129 (2007) 8678-8679.

Photoswitchable Molecular Glue for DNA, C. Dohno, S. Uno, and K. Nakatani, *J. Am. Chem. Soc.* 129 (2007) 11898-11899.

Polyamines stabilize left-handed Z-DNA: Using X-ray crystallographic analysis, we have found a new type of polyamine (PA) that stabilizes left-handed Z-DNA, H. Ohishi, M. Odoko, K. Grzeskowiak, Y. Hiyama, K. Tsukamoto, N. Maezaki, T. Ishida, T. Tanaka, N. Okabe, K. Fukuyama, D.-Y. Zhou, and K. Nakatani, *Biochem. Biophys. Res. Commun.* 366 (2008) 275-280.

The crystallographic study of left-handed Z-DNA d(CGCGCG)<sub>2</sub> and thermine complexes crystallized at various temperatures and at various concentration of cations, H. Ohishi, M. Odoko, D.-Y. Zhou, Y. Tozuka, N. Okabe, K. Nakatani, T. Ishida, and K. Grzeskowiak, *Biochem. Biophys. Res. Commun.* 368 (2008) 382-387.

Ligand-Stabilized Hairpin Structures Interfered with Elongation of Human Telomere, M. Hagihara, Y. Goto, and K. Nakatani, *ChemBioChem.* 9 (2008) 510-513.

### **International Conferences**

Design and Evaluation of Bivalent Enzyme Inhibitors for Simultaneous Recognition of Interior and Exterior Protein Surfaces, \*J. Ohkanda, S. Machida, and N. Kato, Gordon Research Conference, Bioorganic Chemistry, New Hampshire, USA, June 10-15, 2007.

An Unusual Chimera Diterpene Synthase Is Responsible for Fusicoccin Biosynthesis, \*T. Toyomasu, M. Tsukahara, A. Kaneko, R. Niida, C. Ikeda, W. Mitsuhashi, T. Daiiri, N. Kato, and T. Sassa, 19th International Conference on Plant Growth Substances, Rivera Maya, Cancun, Mexico, July 21-25, 2007.

Bivalent Inhibitors of Type-I Geranylgeranyltransferase for Simultaneous Recognition of Interior and Exterior Protein Surfaces, \*J. Ohkanda, S. Machida, N. Kato, M. A. Blaskovich, S. M. Sebt, and K. Harada, American Chemical Society 234th National Meeting, Boston, USA, August 19-23, 2007.

Fusicoccin Derivatives as Therapeutic Agents Based on Induction of Differentiation, \*Y. Honma, M. Akimoto, T. Sassa, and N. Kato, 19th EORTC-NCI-AACR Symposium on "Molecular Targets and Cancer Therapeutics", San Francisco, USA, October 22-26, 2007.

Synthesis and Evaluation of VIS-Sensitive Azobenzene Derivatives for Controlling Cellular Gene Expressions, \*K. Kaihatsu, S. Sawada, and N. Kato, 11th Sanken International Symposium, Awaji, Japan, February 2-4, 2008.

Synthesis of Green Tea Catechin Derivatives and Evaluation of Their Anti-influenza Virus Activity, \*S. Mori, S. Miyake, K. Kaihatsu, and N. Kato, 11th Sanken International Symposium, Awaji, Japan, February 2-4, 2008.

Dual Inhibitors of Protein Prenyltransferase: Activity-tuning by Target Protein Surfaces, \*S. Machida, N. Kato, and J. Ohkanda, 11th Sanken International Symposium, Awaji, Japan, February 2-4, 2008.

Synthesis and Biological Evaluation of Fusicoccin Derivatives, \*T. Inoue, Y. Maruyama, H. Nitta, J. Ohkanda, and N. Kato, 11th Sanken International Symposium, Awaji, Japan, February 2-4, 2008.

Single Molecule Studies on F<sub>1</sub>-ATPase, \*H. Noji, 3rd Work Shop of the UK-Japan Bionanotechnology Collaboration, Oxford, UK, July 19, 2007.

Rapid detection of drug efflux from single bacterial cell enclosed in femtoliter chamber

array, \*R. Iino, K. Nishino, M. Nakata, E. Nikaido, Y. Matsumoto, S. Sakakihara, S. Takeuchi, A. Yamaguchi, and H. Noji, Micro Total Analysis Systems 2007, Paris, France, October 7-11, 2007.

Versatile Acrylamide-based Microchambers for Single Molecular Biological Assays and Analysis, \*L. Lam, S. Sakakihara, K. Ishizuka, S. Takeuchi, and H. Noji, Micro Total Analysis Systems 2007, Paris, France, October 7-11, 2007.

Single Molecule Studies on F<sub>1</sub>-ATPase, \*H. Noji, Autumn School for PhD Students and Young Researcher (NAMIS) 2007, Tokyo, Japan, November 5, 2007.

Single Molecule Studies on F<sub>1</sub>-ATPase, \*H. Noji, The 6th JSPS Forum in France, "Chemical and Physical Nanobiology for Medicine", Strasbourg, France, November 23, 2007.

ATP-driven Rotation of FoF<sub>1</sub>-ATP Synthase Reconstituted into Supported Membrane. \*R. Iino, K. V. Tabata, H. Ueno, R. Hasegawa, and H. Noji, The Joint Biophysical Society 52nd Annual Meeting and 16th International Biophysics Congress, California, USA, February 2-6, 2008.

Fluorescence Imaging of Intracellular ATP Using A FRET-based Probe. \*H. Imamura, K. Saito, K. P. H. Nhat, R. Iino, Y. Yamada, T. Nagai, and H. Noji, The Joint Biophysical Society 52nd Annual Meeting and 16th International Biophysics Congress, California, USA, February 2-6, 2008.

Single Molecule Studies on F<sub>1</sub>-ATPase, \*H. Noji, International Symposium on Hierarchy and Holism (ISHH), "Bridging across Different Hierarchies in Natural Sciences", Okazaki, Japan, February 23, 2008.

Mismatch-Binding Ligands as a Molecular Glue for DNA, \*C. Dohno, T. Peng, and K. Nakatani, 7th International Meeting on Recognition Studies in Nucleic Acids, Sheffield, UK, April 1-5, 2007.

Photoswitchable Mismatch-Binding Ligands Control DNA Hybridization, C. Dohno, S. \*Uno, M. Oku, and K. Nakatani, 7th International Meeting on Recognition Studies in Nucleic Acids, Sheffield, UK, April 1-5, 2007

Mismatch-Binding Ligands: Chemistry Approach to Genotyping, \*K. Nakatani, International Symposium on Advanced Functional Genomics, Kazusa DNA Research Institute, Chiba, Japan, October 11, 2007.

Molecular Glue for DNA, \*K. Nakatani, The 13th Korea-Japan Seminar on Organic Chemistry, Department of Chemistry, KAIST, Daejeon, Korea, October 20-21, 2007.

Reversible regulation of binding between a photoresponsive peptide and its RNA aptamer, \*G. Hayashi, M. Hagihara, C. Dohno, M. Oku, and K. Nakatani, 5th International Symposium on Nucleic Acids Chemistry, Tokyo, Japan, November 20-22, 2007.

Reversible Control of DNA Hybridization by Photoresponsive Ligands, \*S. Uno, C. Dohno, M. Oku, and K. Nakatani, 5th International Symposium on Nucleic Acids Chemistry, Tokyo, Japan, November 20-22, 2007.

Application for the Fluorescent Detection of Single Nucleotide Difference using Cytosine Bulge Hairpin Primers, \*F. Takei, M. Hagihara, Y. Oka, and K. Nakatani, 11th Sanken International Symposium, Awaji, Japan, February 2-4, 2008.

Switching DNA hybridization by a molecular glue for DNA, \*T. Yamamoto, C. Dohno, S. Uno, and K. Nakatani, 11th Sanken International Symposium, Awaji, Japan, February 2-4, 2008.

Displacement Assay For RNA-ligand Interactions, Using Ligand's Fluorescent Property, \*S. Umemoto, J. Zang, and K. Nakatani, 11th Sanken International Symposium, Awaji, Japan, February 2-4, 2008.

### **Contributions to International Conferences and Journals**

N. Kato                      24th Conference on Combinatorial Chemistry, Japan  
                                    (Conference Director)  
N. Kato                      25th Conference on Combinatorial Chemistry, Japan  
                                    (Organizing Committee)

### **Publications in Domestic Meetings**

|                                                                |           |
|----------------------------------------------------------------|-----------|
| Japan Chemical Society Meeting                                 | 14 papers |
| Biophysical Society of Japan                                   | 11 papers |
| Japan Bioenergetics Group                                      | 4 papers  |
| Japanese Society for Chemical Biology Meeting                  | 3 papers  |
| Japan Society for Bioscience, Biotechnology, and Agrochemistry | 3 papers  |
| Symposium on Nucleic Acids Chemistry                           | 2 papers  |
| Meeting of West Japan Branches of Japan Chemical Society       | 2 papers  |
| SORST Joint Symposium                                          | 2 papers  |
| Supported Membrane Workshop                                    | 2 papers  |
| Informal Symposium on Organic Reactions                        | 2 papers  |
| Symposium on Biofunctional Chemistry                           | 1 paper   |
| The Japanese Cancer Association                                | 1 paper   |
| Symposium on Photochemistry                                    | 1 paper   |
| RNA Meeting 2007                                               | 1 paper   |
| The Pharmaceutical Society of Japan                            | 1 paper   |
| Symposium on the Chemistry of Biocatalysis                     | 1 paper   |
| Japanese Society for Biomaterials                              | 1 paper   |
| Chem-Bio Informatics Society                                   | 1 paper   |
| Forum on Biomolecular Chemistry                                | 1 paper   |

### **Sponsorship**

#### **Grant-in-Aid for Scientific Research on Priority Areas**

|         |                                           |             |
|---------|-------------------------------------------|-------------|
| H. Noji | Rotational mechanism of FoF1-ATP synthase | ¥49,800,000 |
|---------|-------------------------------------------|-------------|

**Grant-in-Aid for Scientific Research (S)**

|             |                                                                                      |             |
|-------------|--------------------------------------------------------------------------------------|-------------|
| K. Nakatani | Regulation of DNA Structure and Function<br>Based on the Stabilization of DNA Duplex | ¥34,500,000 |
|-------------|--------------------------------------------------------------------------------------|-------------|

**Grant-in-Aid for Scientific Research (A)**

|         |                                                                                                        |             |
|---------|--------------------------------------------------------------------------------------------------------|-------------|
| H. Noji | Development of novel single molecule<br>measurement method using ultra-small reaction<br>chamber array | ¥15,600,000 |
|---------|--------------------------------------------------------------------------------------------------------|-------------|

**Entrusted Research**

|         |                                                                                        |                                                                                                           |             |
|---------|----------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|-------------|
| N. Kato | Program for<br>Promotion of<br>Fundamental<br>Studies in<br>Health Sciences<br>(NIBIO) | Development of new anti-<br>cancer agents based on the<br>differentiation-inducing<br>diterpene glycoside | ¥34,000,000 |
|---------|----------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|-------------|

# **Intelligent Artificial Agents and Information Systems Inspired by Biological System Dynamics**

Specially Appointed Professor: Toshio KAWAHARA  
Specially Appointed Associate Professor: Naoki ASAKAWA  
Specially Appointed Assistant Professor: Teruo KANKI  
Specially Appointed Assistant Professor: Yasushi HOTTA

## **Outlines**

“Intelligent Artificial Agents and Information Systems Inspired by Biological System Dynamics” (“Yuragi Project”) forms the innovation center as the project of the “Formation of Innovation Center for fusion of Advanced Technologies”. In Yuragi Project, in cooperation with participating private companies, we seek to create new intelligent artificial agents and information systems that implement highly flexible functions currently unique to living organisms.

Our strategy for achieving this goal is first to elucidate the mechanisms of expressing function in biological systems via active applications of biodynamics, that is, to understand the intrinsic stochastic and fluctuating nature of biological systems. Specifically, we will measure and analyze “dynamical fluctuations” which make biological functions highly robust and flexible. From this, we will establish new applications based on the novel principles elucidated from biological energy conversion and information processing. Incorporating knowledge from such research, new nano-materials science, information systems science, and robotics will be established. We wish to contribute to the creation of new basic and applied sciences that are capable of responding to the needs of an increasingly information-driven society.

The key concept in Yuragi project is an attractor selection model, where attractor dynamics are modified by the environmental activity under the fluctuation. We reveal the structure of the attractor selection devices inspired by stochastic resonance model, and study the nature of such stochastic devices. Then, nano materials suitable for the attractor selection devices using fluctuation mechanism are developed with the process methods and functions. And also we will develop the novel techniques for the evaluation of dynamical fluctuations.

## **Current Research Project**

### **Design of attractor switching devices based on stochastic resonance**

We have designed a novel class of noise driven attractor switching devices that are based on stochastic resonance phenomenon. Two devices, a learning/memory/forgetting device and *Yuragi* attractor switching devices, are designed using numerical simulation. The devices are composed of the delayed directional, circular coupling of stochastic resonant device elements. The single stochastic resonant device element is composed of signal inputs, a noise generator, a signal adder, and a comparator.

### **Yuragi Oscillator with Stochastic Resonance**

Biological systems functionally utilize stochastic processes to induce fluctuation for the

whole of the system states, achieving flexibility and robustness for the system response. In this study, we demonstrate to induce such fluctuation in an oscillator by using stochastic resonance which has been considered as origin of the stochastic process. The oscillator showed free-running oscillation with fluctuation by only adding noise. Furthermore, it could adaptively tune oscillation frequency when an external signal is input.

### **Room-temperature-photoinduced magnetism and spin-electronic functions of spinel ferrite with a spin-cluster structure**

Room-temperature-photoinduced magnetization (PIM) was observed in spinel ferrite  $\text{Al}_{0.2}\text{Ru}_{0.8}\text{Fe}_2\text{O}_4$  thin films with a spin-cluster-glass structure. Additionally, the films exhibited significant properties as spintronic materials, showing a low saturation magnetization under  $0.6\mu_{\text{B}}$  /unit cell and good conductivity with a high spin polarized electron level of over 75%. A combination of high-temperature PIM and the electronic properties associated with spintronics would generate an area of research and development that utilize the degrees of freedom offered by optical systems in the field of spintronics. Then there is a possibility for conversion of magnetic fluctuation due to spin-cluster glass into electric property, which would be a promising feature for making “yuragi” electronic devices.

### **Fabrication of Co nano clusters for the catalyst of carbon nanotube devices**

Carbon nanotubes (CNTs) have attracted a significant attention for various potential applications in nano devices. CNT sometimes has large noise in itself, which could be used for noise-enhanced signal processing at the nano-level through stochastic resonance, for example. To obtain stable characteristics of applications, the control of the CNT growth is important. As the catalysts such as Co are used for the growth of CNT, the basics of the control of CNT is that of the metal nano particles of Co. Arc plasma gun (APG) can deposit the small size of Co catalyst. In this study, we tried to control the Co cluster size and its distribution. The cluster size can be controlled at a few nano meters depending on the shot pulse number of APG. For the further control of the size distribution, we reduced the ionized particles in evaporants using the long anode in the gun. Finally, we can obtain the small distribution of cluster size with a few nano meters.

## **Publications**

### **Original Papers**

Dielectric Properties of  $\text{Ba}(\text{Zr}, \text{Ti})\text{O}_3$  Thin Films Fabricated by Pulsed Laser Deposition, Takanori Hino, Minoru Nishida, Takao Araki, Takahiro Ohno, Toshio Kawahara, Masakazu Murasugi, Hitoshi Tabata and Tomoji Kawai: Journal of Laser Micro/Nanoengineering, 2 (3) (2007) 166-169.

Possibility of reverse Monte Carlo modelling for hydrogenated amorphous Si deposited on reactive ion etched Si substrate, Toshio Kawahara, Yoshinori Matsui, Seiichi Tagawa, Tomoji Kawai and Hideki Matsumura: J. Phys.: Condens. Matter, 19 (2007) 335211.

STM tip-enhanced photoluminescence from porphyrin film, R. Nishitani, H. W. Liu, A.

Kasuya, H. Miyahira, T. Kawahara, H. Iwasaki: Surface Science, 601 (2007) 3601-3604.

Fabrication of functionally graded bulk materials of organic polymer blends by uniaxial thermal gradient, S.Koide, K.Yazawa, N.Asakawa, Y.Inoue: J.Mater.Chem., 17 (2007) 582-590.

Influence of a Melt Flow on Generation of functionally Graded Structure in Bulk Polymeric Materials under Uniaxial Thermal Gradient, S.Koide, N.Asakawa, Y.Inoue, K.Yazawa: Macromol.Chem.Phys., 209 (2008) 499-507.

The Dynamic Structure of Regioregulated Poly(4-methylthiazole-2,5-diyl), S.Mori, T.Yamamoto, N.Asakawa, K.Yazawa, Y.Inoue: Polymer J., 40 (2008) 475-478.

Characterization of LaVO<sub>x</sub> thin films by photoemission spectroscopy, H. Wadati, Y. Hotta, M. Takizawa, A. Fujimori, T. Susaki, and H. Y. Hwang: J. Appl. Phys., 102 (2007) 53707.

Asymmetric interface profiles in LaVO<sub>3</sub>/SrTiO<sub>3</sub> heterostructures grown by pulsed laser deposition, L. Fitting Kourkoutis, D. A. Muller, Y. Hotta, and H. Y. Hwang: Appl. Phys. Lett., 91 (2007) 163101.

Polar discontinuity doping of the LaVO<sub>3</sub>/SrTiO<sub>3</sub> interface, Y. Hotta, T. Susaki, and H. Y. Hwang: Phys. Rev. Lett., 99 (2007) 236805.

Hard x-ray photoemission study of LaAlO<sub>3</sub>/LaVO<sub>3</sub> multilayers, H. Wadati, Y. Hotta, A. Fujimori, T. Susaki, H. Y. Hwang, Y. Takata, K. Horiba, M. Matsunami, S. Shin, M. Yabashi, K. Tamasaku, Y. Nishino, and T. Ishikawa: Phys. Rev. B, 77 (2008) 45122.

### **Review Papers**

Exotic physical properties at interfaces of transition metal oxide, Y. Hotta and H. Y. Hwang: Parity 23(1) (2008) 30-33 (in Japanese).

### **Patents**

Stochastic Resonance Rings Devices, Stochastic Resonance Ring Networks Devices, Learning/memory Storage/forgetting Devices, Attractor Switching Devices, and Stochastic Resonance Units, N. Asakawa, Y. Hotta, T. Kanki, T. Kawahara, T. Kawai, and H. Tabata: Japanese Patent Application Number, 2007-215458.

Magnetic Memory Device Assisted by Light, T. Kanki, T. Kawahara, Y. Fujiwara, T. Kawai, Y. Terai, Y. Hotta, N. Asakawa, M. Seki: Japanese Patent Application Number, 2007-228376.

Yuragi Oscillator, Yuragi Oscillator System, Device for Observation, and Control System Using Yuragi Oscillators, Y. Hotta, T. Kanki, N. Asakawa, T. Kawahara, T. Kawai, and H. Tabata: Japanese Patent Application Number, 2007-215457.



### International Conferences

Size and distribution control of Co nano clusters grown by arc plasma gun, \*Toshio Kawahara, Teruo Kanki, Yasushi Hotta, Naoki Asakawa, Tomoji Kawai, Hitoshi Tabata: 9th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN9), Tokyo, Japan, Nov. 11-15, 2007.

Magneto-Electric Properties of Photoinduced Magnet (Al,Ru,Fe)O<sub>3</sub> Thin Films (poster), \*T.Kanki, Y.Hotta, N.Asakawa, T.Kawahara, H.Tabata, T.Kawai: The 14th International Workshop on Oxide Electronics, Jeju island, Korea, October 7-10, 2007.

Epitaxial growth of spinel ferrite oxide (Al,Ru,Fe)<sub>3</sub>O<sub>4</sub> on a GaAs(001) substrate using a MgO buffer layer (poster), \*T.Kanki, T.Kawahara, N.Asakawa, Y.Hotta, Y.Terai, Y.Fujiwara, H.Tabata, T.Kawai: 2007 MRS Fall Meeting, Boston, USA, Nov. 26-30, 2007.

### Publications in Domestic Meetings

|                                                                       |          |
|-----------------------------------------------------------------------|----------|
| The Japan Society of Applied Physics                                  | 4 papers |
| The Society of Polymer Science, Japan                                 | 1 paper  |
| The Institute of Electronics, Information and Communication Engineers | 2 papers |

### Sponsorship

#### Entrusted Research

|          |                                                                |                                                                          |             |
|----------|----------------------------------------------------------------|--------------------------------------------------------------------------|-------------|
| T. Kawai | Ministry of Education, Culture, Sports, Science and Technology | Intelligent Artificial Agents and Inspired by Biological System Dynamics | ¥86,856,399 |
|----------|----------------------------------------------------------------|--------------------------------------------------------------------------|-------------|

# **Activities of Facilities**

## Workshop

Director Professor: Goro ISOYAMA

Technical Staff

Machine Shop: Michiaki KAKUICHI, Masayoshi OHNISHI

Glassworks: Hiroaki MATSUKAWA, Noriyuki OGAWA

## Outlines

A machine and carpentry shop and a glass factory, which are predecessors of the Workshop, were set up when the Institute of Scientific and Industrial Research was founded. The machine and carpentry shop and the glass factory were unified to be the Workshop when the Technical Division was established in 1982. Since research fields studied in the institute covers a wide range, many of experimental apparatuses requested to the Workshop are various and novel. The Workshop, which consists of the Machine Shop and the Glassworks, plays an important role in activities of the institute and contributes to them by making and providing such experimental apparatuses.

The Machine Shop performs design and trial manufacture of experimental apparatuses for science and engineering as well as production of experimental tools made of various metals. Requests of experimental apparatuses for ultra high vacuum or ultra low temperature are increasing recently and accordingly we work in closer cooperation with researchers asking such apparatuses from the design phase to respond to the requests and make apparatuses best fit to experimental purposes. A gate-type machining center was introduced in 2002, so that we can answer to advanced and difficult requests from researchers. A corner of the machine shop for joint-use, called an open shop, is attached and we coach researchers in technique properly.

The Glassworks performs design and trial manufacture of experimental tools and apparatuses made of various kinds of glass. We develop apparatuses necessary and suitable for experiments and we also devote ourselves to our studies and establishment of technique for improving functions of conventional apparatuses and for providing safer and easier-to-use apparatuses. Since we are recently asked to work with ceramics, and a quartz glass product of high quality, we are trying to obtain machines for it.

## Activities

We continued an open house of the Workshop for the Festival of Osaka University called Ichō-Sai. The machine shop showed machine tools, displayed experimental apparatuses being made, and held a practice course of carved seals. The Glassworks showed a glass lathe and experimental apparatuses being made, displayed objects d'art associated with science, and also gave demonstrations of glass processing by handwork and held a practice course.

We renewed a drill press and a work station for CAD for the Machine Shop and an internal grinder for the Glassworks of the Work Shop in the fiscal year 2007. We also equipped the Machine Shop with peripheral devices and tools for the machining center for precise machining.

The Glassworks receives staff members of universities in the Kansai area for technical training in glass work and in 2007 it received a person from Kobe University and coached him for handing skills and technique down to the next generation.

### 1. Number of jobs

Machine Shop: 254 jobs (228 jobs in the previous year).  
Glassworks: 209 jobs (240 jobs).

**2. Number of users in the open shop**

Machine Shop: 50 users.  
Glassworks: 20 users.

**3. Number of visitors during Icho-Sai**

Machine Shop: 70 persons (60 persons in the practice course).  
Glassworks: 200 persons (180 persons).

**4. Number of persons being trained**

Machine Shop: 11 persons.  
Glassworks: 5 persons for 18 subjects, including 12 subjects out of the institute.

## **Office of Information Network**

|                      |                                              |
|----------------------|----------------------------------------------|
| Professor,Director:  | Katsuaki SUGANUMA                            |
| Professor:           | Kazuhiko NAKATANI                            |
| Assistant Professor: | Kouzou OHARA                                 |
| Assistant Professor: | Keun-Soo KIM                                 |
| Technical Staffs:    | Takanori TANAKA, Senjin AIHARA, Yuka OKUMURA |
| Supporting Staff:    | Miyu SAKAMOTO                                |

### **Outline**

Office of Information Network was inaugurated in March, 1999, to organize the operation of the information network in ISIR, which had been started with support by volunteers, because of the rapid spread of the information network and the growth of its importance in the research environment. The information was constructed as a prototype by the departments in the division of Intelligent System Science in the late 1980's and has been expanded to the whole of ISIR with the development of ODINS (Osaka University Information Network System). Recently it has played an important role in ISIR to release/access the information available in the Internet. Office of Information Network is now supporting researchers and students on the variety areas.

## Laboratory for Radio-isotope Experiments

Professor: Akihito YAMAGUCHI

### Outline

This laboratory is specially designed for biochemical and molecular biological experiments using radioactive compounds labeled with  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{32}\text{P}$ ,  $^{33}\text{P}$ ,  $^{35}\text{S}$ . The main equipments are liquid scintillation counters and an image scanner. This laboratory is essential for the research in the field of biochemistry, molecular biology, and cell biology. Contributions of the facilities to each project are described in the section of each department. The use of radioisotopes is regulated with the national law for the prevention of radiation hazard. The facilities are inspected regularly with authorities and pass the required standard. Radioisotope users are mandatory to be educated every year to get the knowledge for the safe use of radioisotopes.

## Library

Professor: Hiroshi IWASAKI  
Staff: Yasuko ONO  
Supporting Staff: Kuniko HAMANAKA

### Outline

The ISIR Library houses technical books and journals for researchers. Most materials are on open shelves directly available to faculty and students. The library has two reading rooms and a workroom with photocopiers on the second floor of the administration building, and the storage facility on the first floor of the research building.

The library office offers the following services; orders for books and magazines, survey and inquiry of literature, Interlibrary Loan services, photocopy request, and so on.

Guide to the Library could be found on its home page  
(<http://www.sanken.osaka-u.ac.jp/labs/lib-web/>).

(As of April 1, 2008)

|          | Number of books | Journals  | Newspapers |
|----------|-----------------|-----------|------------|
| Japanese | 12222           | 234titles | 4 titles   |
| Foreign  | 43174           | 956titles | 1 title    |

## **Academia Industry Relations Office**

Director, Specially Appointed Professor: Hirokazu Shimizu, Ph.D.

### **Outlines**

The Academia Industry Relations Office (AIR Office) of the Institute of Scientific and Industrial Research (ISIR), is dedicated to reinforcing collaboration between ISIR and the industrial community, thereby combining and developing research potential of the two sectors and promoting activities for new industrial creation and innovation. The AIR Office organizes a variety of activities to inform the industrial community of the ISIR's research efficiently through the interaction with the industrial community such as SANKEN Techno Salon (four times a year) and various Lectures events, and studies on prediction of new industry, novel system of new Industry generation, and intellectual property.

The major activities of AIR Office are: 1) A network development between ISIR and Industry, 2) Responding to inquiries from industry, 3) A liaison between academia and industrial research activities, 4) Creation of complementary opportunities for science and technology progress. AIR Office will make proposals for new business opportunity between academia and industry. New venture business activities and novel industrial products are the vision of AIR Office.

### **Achievements**

#### **Liaison between academia and industrial research activities and Responding to inquiries from industry**

- 1) SANKEN Techno Salon: Quarterly seminar and get-together
- 2) WEB site
- 3) WEB promotion through outsourcing

#### **Supporting Technology Transfer**

- 1) Study groups for the new industry generation
- 2) Investigation of interest group on ISIR's Patents

#### **Coordination of collaboration, contract research and projects with a company**

#### **Coordination of industry-academia collaborative research and development**



## **projects supported by public assistance system**

### **A network development between ISIR and Industry**

Visiting industrial entities, Exhibition of ISIR activities at various meeting, and participating to the various academic meetings and symposiums.

### **Others**

#### 1) Invited Talk

Key factors and efforts for University-corporate networking, H.Shimizu, 2007 Integration Conference on Cooperate-University Network Activation, Gyeongsangnam, Korea, November 27(2007)

2) Promotion of ISIR research activities at Exhibitions such as International Nanotechnology Exhibition (Nano Tech 2008).

## **Public Relations Office**

Director, Professor:       Akihito YAMAGUCHI  
Supporting Staff:         Noriko MATSUMOTO

### **Outline**

Public Relations Office was opened on February 1, 2006. We provide the right information of our Research Institute for the public effectively. The major activities of Public Relations Office are: 1) To collect any required file to generate the basic plan of the publicity, 2) To support editing and issue the Memoirs of ISIR (annual report) and publications, 3) To collect any requires document for creating and editing of official WEB of ISIR, 4) To perform Press Release except the subjects related to the section of general affairs, 5) To collect and preserve of any press release related to ISIR.

## **Technical Division**

Head: Takeshi ISHIBASHI

### **Outlines**

The Technical Division was established in 1982 to deal with professional duties providing better service for researchers. In the ISIR organization, the technician group is independent of the management and the research groups. The organization was the first one among similar organizations established in the national universities of Japan. The Division consists of two groups: Group of Machine and Group of Measurement, in which each group has two sections: Section of Machine/Circuit, Section of Glass in Group of Machine and Section of Measurement/Information, Section of Analysis/Data in Group of Measurement. The technicians work at various places: the Analysis Center, the Workshop, the Office of Information Network, the Electronic Processing Laboratory and the Nanotechnology Center. The Division gives not only high-quality service to research groups but technical training to the researchers and students. The annual report is published to help and encourage training and activities of the members of the Division. In addition, the Division has started the safety lecture for utilizing various machines in the ISIR since 2004. The Technical division makes every effort to promote the ISIR more important development under an independent administration system.

## **Administrative Office     (30-May , 2008)**

Director :                Noboru NAKATA

### **General Affairs Division**

Staffs :                Osamu MIZUGUCHI  
                             Akira KAMATANI  
                             Masahito KAWAZOE  
                             Kazuhisa YAMASAKI  
                             Hiroaki HANAOKA

Supporting Staff:    Emiko KITAURA  
                             Keiko KOJIMA  
                             Ruri MAEKAWA  
                             Yukie YAMADA  
                             Sachiko MITSUMORI  
                             Kazumi HAYASHI  
                             Aya NISHIDA

### **Research Cooperation Division**

Staffs :                Katsumi UEDONO  
                             Shigeo KASHIWAKURA  
                             Namiko NAKAO  
                             Tetsuya Mori  
                             Yuji SORIHASHI  
                             Akemi KIDA  
                             Katsunori KANAI  
                             Yoichi NAKAHARA  
                             Satoshi YAMAGUCHI

Supporting Staff :    Misako SHIMIZU  
                             Mari KONISHI  
                             Masako OSUGI  
                             Tamiko SHINDE  
                             Hiroko YAMAUCHI  
                             Misato KUBO  
                             Kumiko TERADA  
                             Mayuko TSUDA