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# Ultraprecision Machining based on Physics and Chemistry

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***Key words:*** perfect surface, ultraprecision machining, elastic emission machining (EEM), atmospheric pressure plasma chemical vaporization machining (P-CVM), hydroxyl electrochemical machining (H-ECM)

The paper overviews research preformed at "Osaka University, Ultra Precision Machining Research Center." It explains in detail the historical background, motivation of the research, and physical concepts of new ultraprecision machining methods; i.e., elastic emission machining (EEM), atmospheric pressure plasma chemical vaporization machining (P-CVM) and hydroxyl electrochemical machining (H-ECM).

## 1. Introduction

Since the fiscal year 1995, the Ministry of Education, Culture, Sports, Science and Technology of Japan (Monbusho) has started a new national program in order to establish distinguished centers for the promotion of the world's most advanced and creative scientific research, the so called "Center of Excellence (COE)" program. The Science Council of Monbusho has selected 6 to 7 projects per year from many proposals in various academic fields to be the COE programs. In 1996, as one of the Monbusho COEs, "Osaka University, Ultra Precision Machining Research Center" was inaugurated with the purpose of the "Creation of Perfect Surfaces." During the 1996 to 2000 fiscal years, the center was requested to contribute to advanced technology and basic science, and to become a research center which shares its academic research results with the world.

The term "Ultraprecision Machining" first appeared in the United States in 1963 in a paper on the machining of an artificial satellite. This paper stimulated Japanese scientists to establish a technical committee on Ultraprecision Machining in the Japan Society for Precision Engineering (the former Japan Society for Precision Machining). The committee was the first to introduce the term "Ultraprecision Machining" in Japan. Triggered by such a move, the first author started his challenge to develop a machining process at the level of an atomic unit. In those days, the mechanical machining process was the best method to obtain high machining accuracy. Although the mechanical machining process could only prepare a surface with a figure accuracy of 0.1 $\mu$m and surface roughness of 0.01 $\mu$m, it was sufficient to produce various mechanical parts. Since the Stone Age, the mechanical machining process has been developing as an important and excellent machining method based mainly on experience and has been contributing to the human society.

There is no doubt that the extreme limit of "Ultraprecision Machining" is the atomic-size (0.2 nm) because the minimum unit of an object is an atom. The first author asked himself, "Can atomic-scale machining be achieved by mechanical machining? Or is there another new machining method to achieve atomic-scale machining?" The first author came to the conclusion, "Atomic-scale machining cannot be achieved by mechanical machining," because it is based on motions and multiplication of defects introduced in the material. Since then, the first author embarked on a journey to try to find a new physical and chemical phenomenon that could be utilized for realizing atomic-scale machining (Fig. 1). At that time, the first author was twenty-five years old. It was thirty-four years ago in an era of mass production in Japan. The author could not conceive of the demands for atomic-scale machining even if it could be realized, and never thought that it would

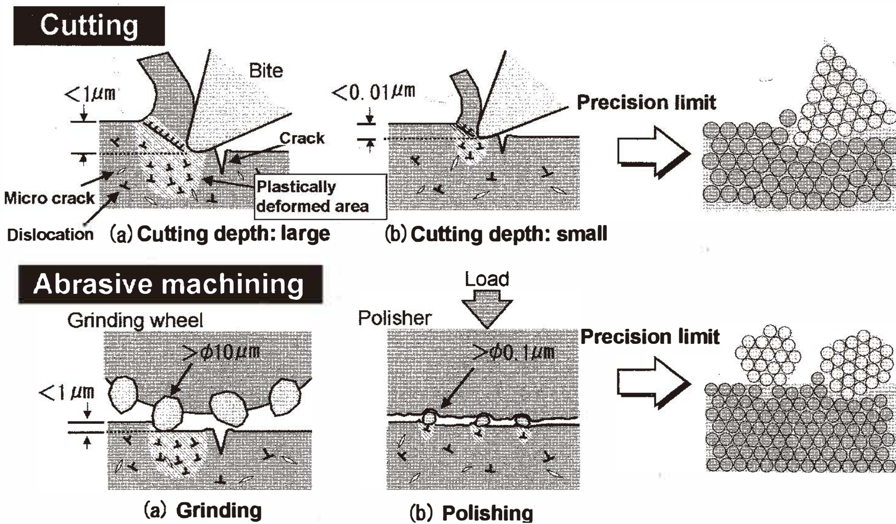



Fig. 1. Limitation of conventional mechanical machining. What happens when atomic-scale cutting depth is employed ?

become useful during his lifetime. In thirty years, however, technological progress has been so remarkable that atomic-scale machining is now indispensable in all areas of advanced technology and basic science. With such a historical background, one of the Monbusho COE projects has been started at the Department of Precision Science and Technology, Osaka University, under the direction of the first author.

## 2. Overview of the Research at Osaka University, Ultra Precision Machining Research Center

The research theme of the Center is "Creation of Perfect Surfaces." Although the term "Perfect Surface" may sound somewhat abstract and nonscientific, the author intended it to have many physical meanings. The term "precise surface" in the past years meant a geometrically flat surface, which is now merely one of the requirements for "perfect surfaces". The "Creation of Perfect Surface (layer)" means that human beings should create a surface with an ideal atomic structure based on the wise providence of the Heaven (physical phenomena) and to find undiscovered electronic properties. In other words, what is required in recent advanced technology is essentially to control electronic properties by the perfect manipulation of the surface atomic arrangement.

### 2.1 *Technology areas requiring perfect surfaces*

Perfect surfaces are required in various areas of advanced technology. Since microroughness on Si substrates affects the device performance, it is predicted that the next generation ULSI (ultra large scale integration) devices will require perfect surfaces that only allow atomic-order roughness. As the substrates of the next generation devices, the SOI (silicon on insulator) wafers should be prepared by ultraprecision machining to leave Si thin films of 10 nm thickness on $SiO_2$. Furthermore, lithography processes for manufacturing these advanced semiconductor devices use short wavelength light sources such as UV excimer lasers or synchrotron radiation.

Therefore, optical components (lenses or mirrors) applicable for short wavelengths should be developed. For UV excimer lasers, aspherical lenses with minimum surface roughness should be developed. For synchrotron radiation in the soft X-ray region, the development of a toroidal-shaped mirror with atomic-scale flatness and ultraprecision figure is desired.

In the area of basic science such as astronomy, ultraprecision machining becomes important to create perfect surfaces for astronomic optics. For example, various astronomical telescopes used for investigating the birth of the universe require perfect surfaced mirrors, and the detection of gravitational waves in gravitational astronomy needs resonance mirrors with more than a few orders higher figure accuracy. Figure 2 shows the application examples that will be machined at the COE center.

### 2.2 *Research objective and contents*

The objectives of the COE are 1) to establish new ultraprecision machining technology that can be used to create atomically flat surfaces with extremely high figure accuracy for arbitrary shapes, 2) to develop a new technology for characterization in order to evaluate

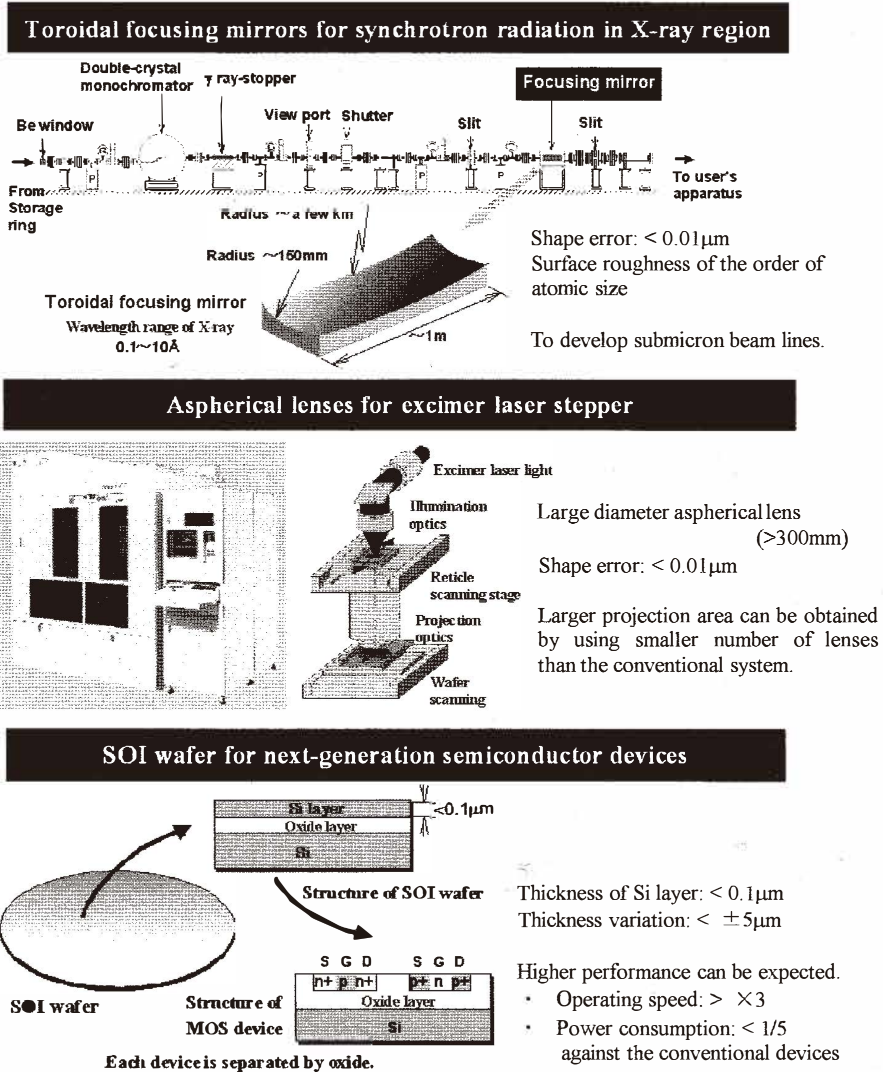



Fig. 2. Application examples which require a perfect surface.

the geometrical and electronic structures of the surface with atomic-level resolution, and 3) to systematize the technology of ultraprecision machining as a new paradigm of natural science.

To achieve these objectives, we pursue goals in the following four research fields that are connected with each other (Fig. 3).

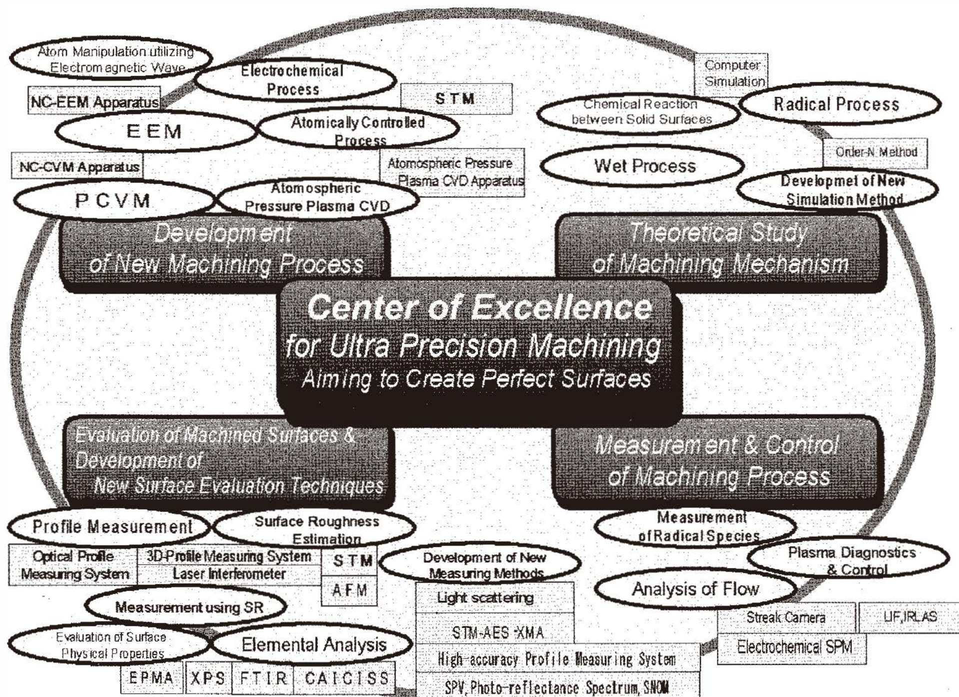



Fig. 3. Research objectives at the Ultra Precision Machining Research Center.

(1) Development of New Machining Process
(2) Theoretical Study of Machining Mechanism
(3) Measurement and Control of Machining Process
(4) Evaluation of Machined Surfaces and Development of New Surface Evaluation Techniques

In the first field (1), a new ultraprecision machining process is developed based on an unprecedented concept different from the conventional mechanical machining. We have achieved elastic emission machining (EEM), atmospheric pressure plasma chemical vaporization machining (P-CVM), hydroxyl electrochemical machining (H-ECM), and rapid thin film growth by atmospheric pressure plasma chemical vapor deposition (P-CVD). In (2), a new molecular-dynamics simulation program is developed based on the first principles of quantum mechanics in order to clarify the machining phenomenon theoretically. In (3), the physical structure of high pressure plasma and hydrodynamics of gas and liquid flow near the surface during machining are analyzed in order to control and optimize machining conditions of P-CVM, P-CVD, and EEM. In (4), the machined surfaces are evaluated by the conventional optical measurements and STM (scanning tunneling microscopy)/STS (scanning tunneling spectroscopy). We are now developing the STM-AES (Auger electron spectroscopy)/XMA (X-ray microanalysis) system to perform atomic-

scale elemental analysis on the surface.

We are proceeding with the various research subjects mentioned above, contributing to the development of advanced science and technology.

## 3. Development of New Ultraprecision Machining Process

### 3.1 *EEM (Elastic Emission Machining)*(1–5)

EEM is the ultimate ultraprecision machining method, and the first author started researching it in 1965 and has been developing it thereafter. EEM utilizes the chemical reaction between two solid surfaces as the machining principle. For example, after two solid materials touch each other and undergo chemical bonding at their interface, one of the solids may bring away the atoms of the other solid surface when they are separated. Machining utilizing this phenomenon is called EEM. When ultrafine powder with sub-micron diameter of an appropriate material is supplied on the work surface along with a flow of ultrapure water, the powder chemically reacts with the work surface (Fig. 4). The powder that reacts with the work surface can remove atoms when it is separated by the ultrapure water flow. The EEM process progresses efficiently when the interfacial electronic state favors the decrease of the back-bond strength of the surface atom. Thus, the EEM process is a chemical reaction between reactive solid surfaces, which is in a contrast with the conventional etching process in liquid solutions. Since the EEM accompanies the weakening of the chemical bonding of the atoms between the surface atom and secondary layers, the surface atoms are removed naturally when the ultrafine powder moves relatively on the work surface. Accordingly, the EEM realizes atomic-scale machining with extremely high accuracy in geometry as well as in the physical properties of the surface.

The elementary process of the chemical reaction during the EEM can be theoretically analyzed with the first-principles molecular-dynamics simulation of quantum mechanics

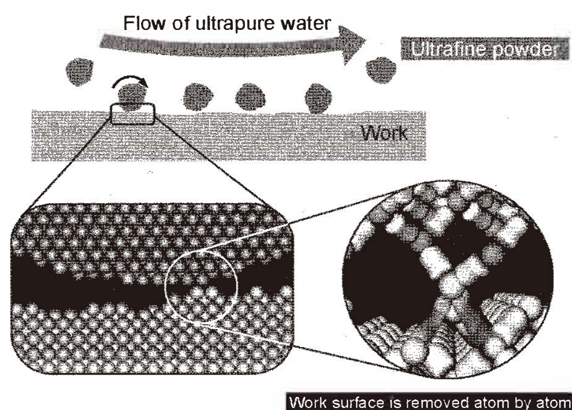



Fig. 4. Removal mechanism of EEM.

as shown in Fig. 5. When $ZrO_2$ and $SiO_2$ particles react with the Si (001) surface, we find that the binding energy between the first and second layers of the Si surface decreases and that the moving powder tends to remove a Si atom from the first layer. The binding energy calculation indicates that $ZrO_2$ particles more effectively remove Si atoms than do $SiO_2$ particles, which agrees with experimental data.

Figure 6 illustrates the numerically controlled (NC) EEM apparatus used in our past experiments. The sheer flow of about 5 m/sec·$\mu$m is produced by bringing the rotating polyurethane sphere toward the work surface in the water dispersed with fine powder until achieving the balance between load and dynamic pressure. The sub-micron fine powder chemisorbing on the surface is moved by the sheer flow accompanying the atoms of the work attached on its surface. NC figuring is accomplished based on the dwelling time dependence of the stock removal by feed speed control of the work table. Figure 7 shows a result of NC machining, which indicates that the high precision machining of the arbitrary figure can be realized with a figure accuracy of 0.01 $\mu$m by NC EEM. STM and phase-shift interferometric observation reveal that peak-to-valley roughness (P-V) of the machined surface is 0.5 nm/60 nm□ and 0.38 nm/330 mm□, respectively. The surface obtained is atomically flat within 2 atomic steps.

Based on these achievements, new NC EEM machines are designed and manufactured to fabricate the optical components shown in Fig. 2. Figure 9 and 10 show NC EEM machines for toroidal-shaped X-ray mirrors that can be used in the synchrotron radiation

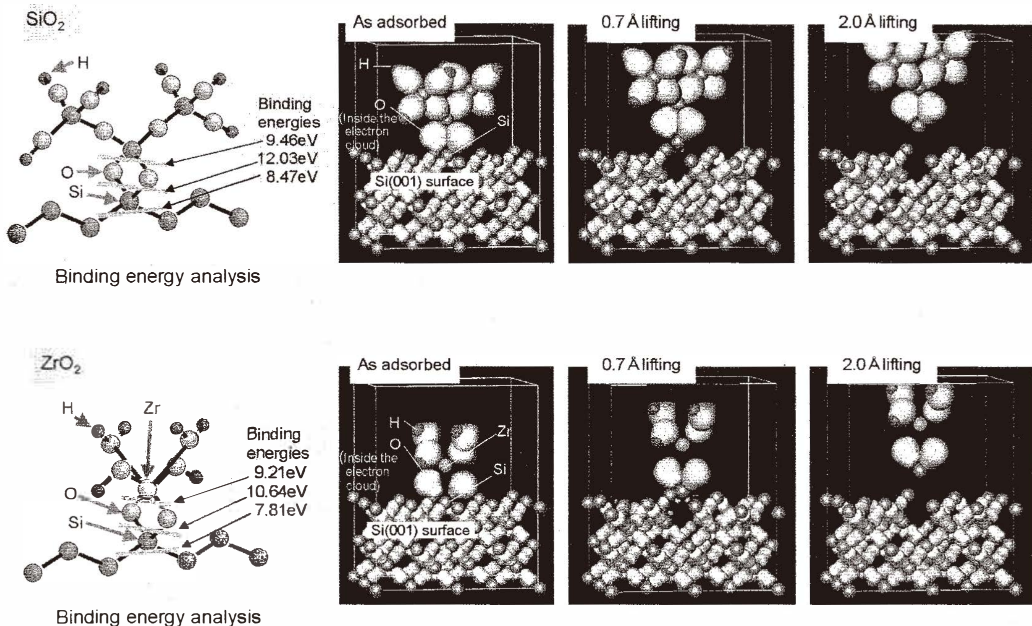
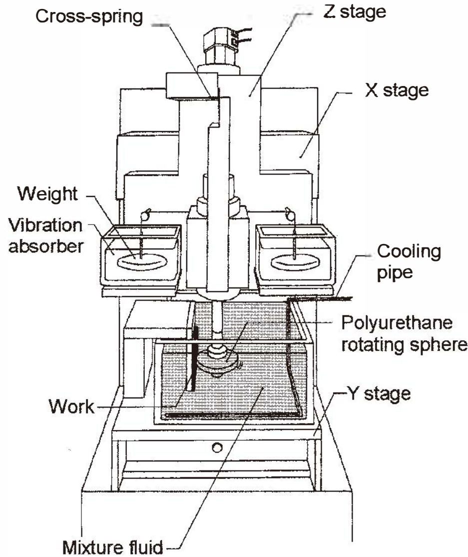
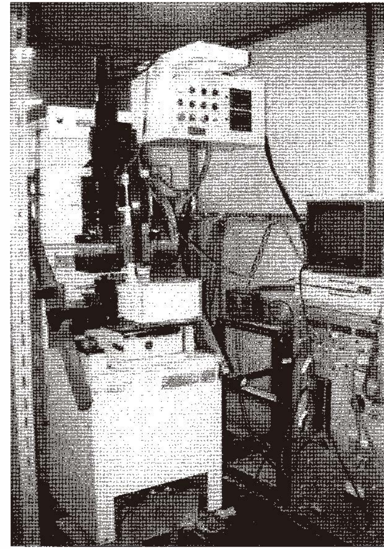


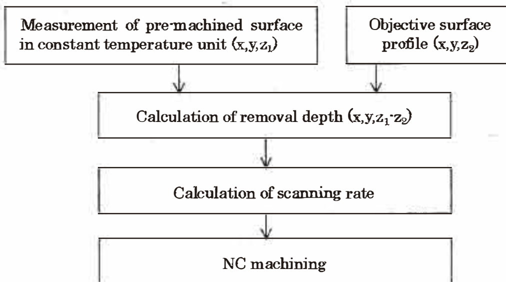

Fig. 5. First-principles molecular-dynamics simulations of EEM processes.

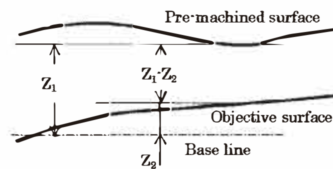



(a) Schematic view of NC EEM apparatus.



(b) Photograph of NC EEM apparatus.



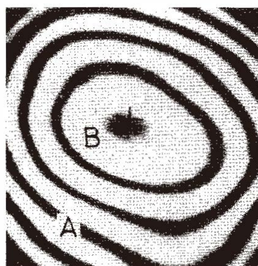

(c) Procedures for NC EEM.

Fig. 6. NC EEM apparatus and machining procedures.

facility and for axi-symmetrical shapes such as aspherical lenses and SOI wafers, respectively. Both machines are designed to operate in ultrapure water using the hydrostatic supporting system for work tables, and to perform machining in ultraclean conditions without exposure to air.

### 3.2 *P-CVM (Plasma Chemical Vaporization Machining)*[6–11]

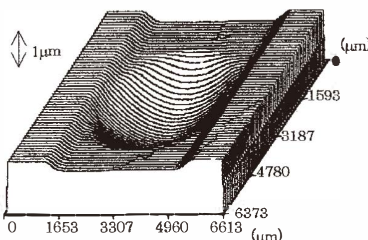
P-CVM utilizes highly reactive neutral radicals (such as halogen atoms with high electronegativity) generated in high-pressure VHF (very high frequency) plasma. The generated radicals react with the surface atoms of the work and transform them into volatile molecules. Figure 11 illustrates the basic mechanism of P-CVM. Because P-CVM is a chemical process that proceeds at the atomic level, a geometrically perfect surface, which



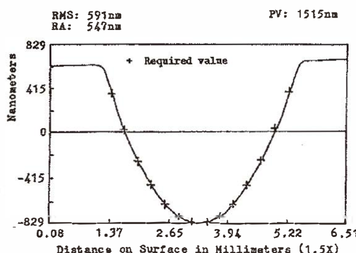

Pre-machined surface

Machined surface

(a) Area A is planarized to the same height of the area around B.
1 fringe : 0.27μm.



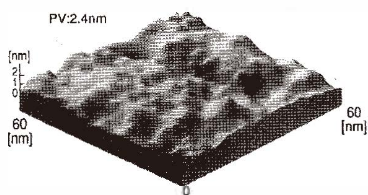

Bird's-eye view of machined surface



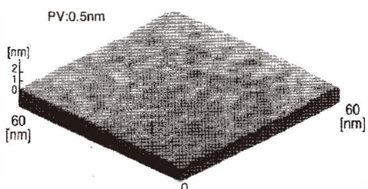

Comparison between machined and objective surface profiles at the centerline.

(b) Spherical surface machining (Pre-machined surface is an optical flat with the accuracy of λ/100).

Fig. 7. Examples of NC EEM.

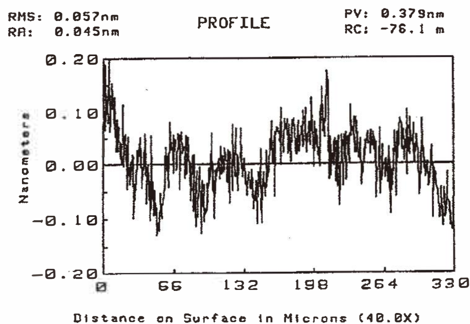



ULSI grade Si wafer surface




EEM surface

(a) STM observation of machined surfaces.




(b) Phase-shift interferometory observation of EEM surface.

Fig. 8. Examples of EEM surfaces.

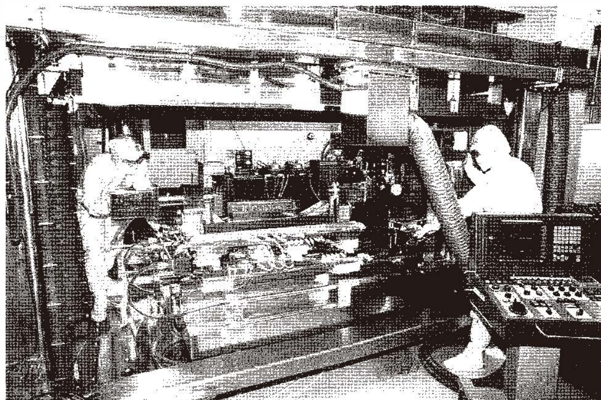


Fig. 9. Photograph of NC EEM machine for toroidal-shape X-ray mirrors.

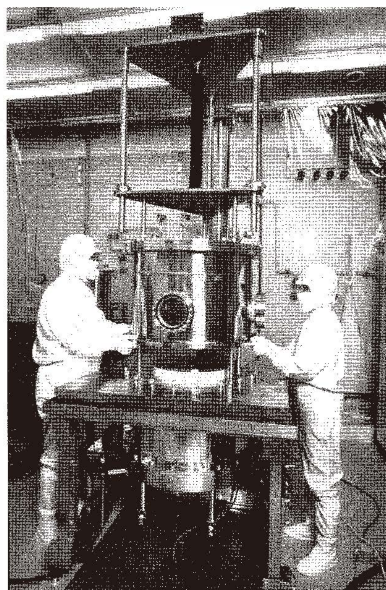


Fig. 10. Photograph of NC EEM machine for axi-symmetrical shape.

is also free from crystallographic or structural damages, can be obtained. A similar machining phenomenon is already utilized in the reactive plasma etching in the LSI manufacturing process. The reactive plasma etching, however, has low machining efficiency and is spatially uncontrollable because it utilizes low-pressure ($1 - 10^{-3}$ Torr) plasma. On the contrary, in P-CVM, high-pressure plasma (higher than 1 atm) is utilized.

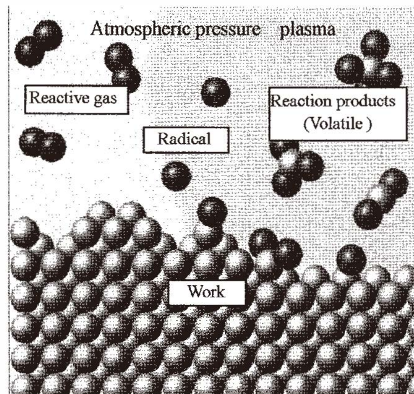



Fig. 11. Basic mechanism of P-CVM.

The VHF high-pressure plasma is localized around the electrode and can generate high-density radicals. The former may realize spatial resolution as high as that in the case of conventional mechanical machining. The latter makes it possible to attain machining efficiency higher than the conventional one.

In an actual P-CVM process, rotary electrodes with high velocity are utilized as shown in Fig. 12. By placing a rotating electrode close to the work surface and by applying VHF power to generate plasma in the gap between the electrode and the work surface, we can proceed with the P-CVM as if a grinding wheel performs mechanical grinding. Rotating an electrode at a high velocity enables one to achieve 1) high supply efficiency of reactive gas; 2) high machining efficiency due to the high power supply mediated by the cooling of the electrode; 3) realization of surface flattening due to the high velocity gas flow in the horizontal direction upon the work surface. The phenomenon 3) occurs due to the unique property related to the viscosity of the high-pressure plasma. By using the power supply of VHF (150 MHz) frequency, amplitude and energy of the ions in the plasma are reduced to 1/100 of the usual 13.56 MHz plasma, and this prevents the surface damage induced by the collision of the ions with the work surface. Special considerations are given to prevent an occurrence of high-temperature arc discharge plasma. We coated the rotary electrode surface with alumina to reduce the thermal effects and to eliminate the secondary electron emission from the electrode.

Next, a P-CVM apparatus in actual use is described. Figure 13 shows a P-CVM apparatus for planarization using the cylindrical rotary electrode. An 8-inch Si wafer can be polished on the work stage equipped with vacuum chucking. The gap between the rotary electrode and the work is controlled by monitoring the transmission intensity of the laser beam. Figure 14 shows a measured roughness of the machined surface. It is found that P-CVM polishing flattens the waviness in the as-received Si wafer. However, because P-CVM utilizes the etching in vapor phase, there must be selectivity of the machining across the work surface. Therefore, it is unconceivable that the surface roughness machined by P-CVM is better than that by EEM. When the ultimate and perfect surface is

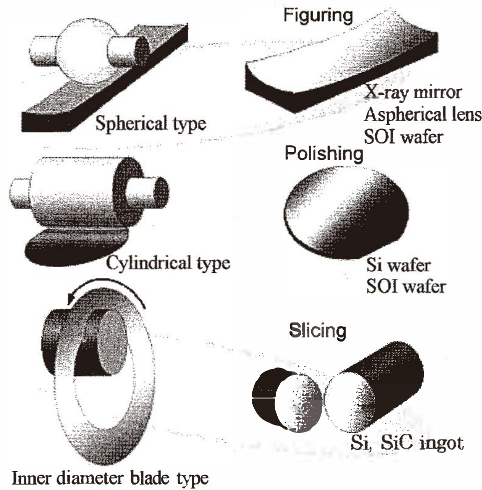



Fig. 12. Various types of rotary electrodes and their application.

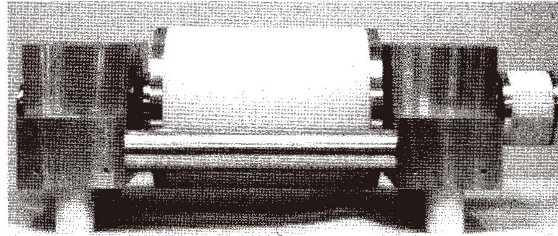
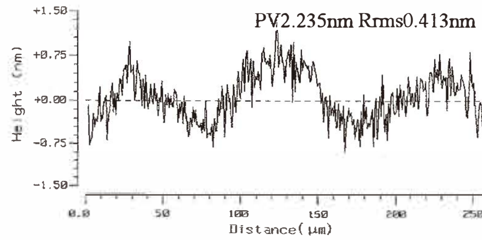


Fig. 13. P-CVM machine for planarization.

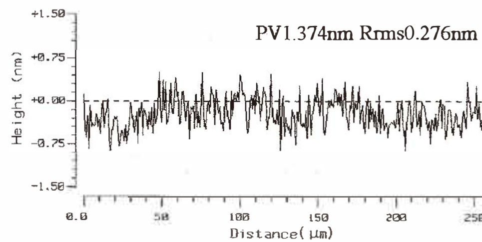
required, we think that pre-machining a surface with highly efficient P-CVM and finishing it with EEM may yield the desired result.

Figure 15 illustrates the P-CVM apparatus used for slicing. Similar to the inner diameter diamond blade used in a conventional slicing machine, a stainless blade of 0.1 mm thickness installed by mechanical tensioning is used as a rotary electrode. In order to slice large-diameter Si wafers with high machining efficiency, it is necessary to make a full-scale machine that has very large inner diameter blades. If it becomes possible to slice large diameter Si wafers without a damaged layer, we can reduce the number of Si wafering processes and construct an ideal machining line for the production of Si wafers. The other targeted objects on which this apparatus can be used are functional materials such as SiC which are difficult to machine by conventional methods.

Concerning various types of three-dimensional figuring, an NC P-CVM machine is being designed and manufactured. Figure 16 shows the procedures of the NC P-CVM, which is the same as the NC EEM that utilizes dwelling time dependence of the stock removal. Highly precise three-dimensional figuring is carried out by feed speed control of




(a)ULSI grade Si wafer surface




(b) Polished surface by P-CVM

Fig. 14. Surface roughness of Si wafer.

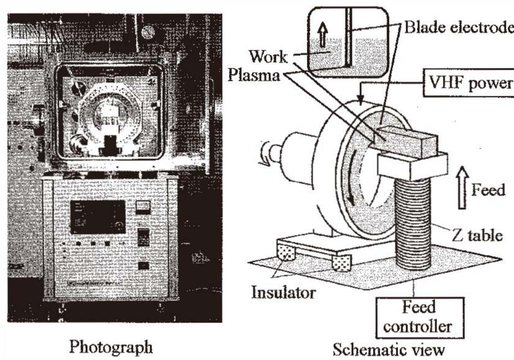



Fig. 15. P-CVM machine for slicing.

the work table. Figure 17 shows a result of three-dimensional figuring by P-CVM. In the atom laser method for separation and concentration of isotopes, it is required to raise the ionization efficiency of uranium isotopes. For this purpose, the beam reshaping mirror shown in Fig. 17 should be prepared to change the profile of the dye laser beam from round to square and the intensity distribution from Gaussian to rectangular. We have succeeded in figuring the beam reshaping mirror in a very complicated three-dimensional shape by NC P-CVM machining.

A large-scale NC P-CVM machine is being developed in order to realize various ultraprecision machinings for the advanced technology area shown in Fig. 2.

Figure 18 shows a NC P-CVM machine suitable for figuring X-ray mirrors for

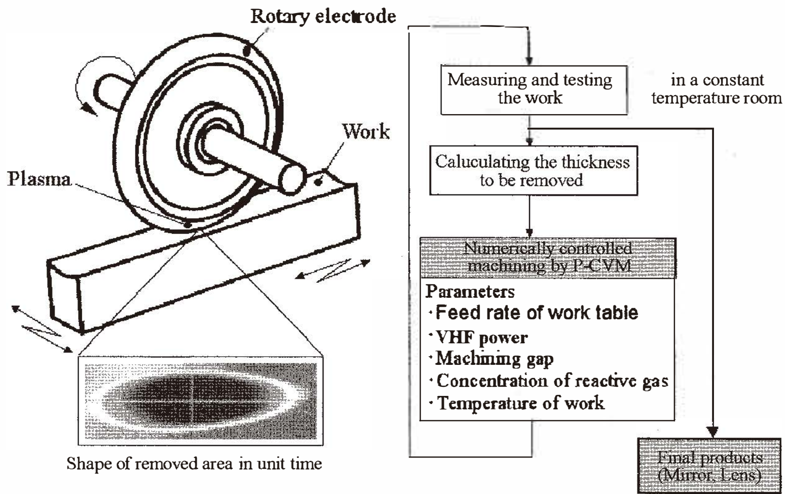



Fig. 16. Procedures of NC P-CVM.

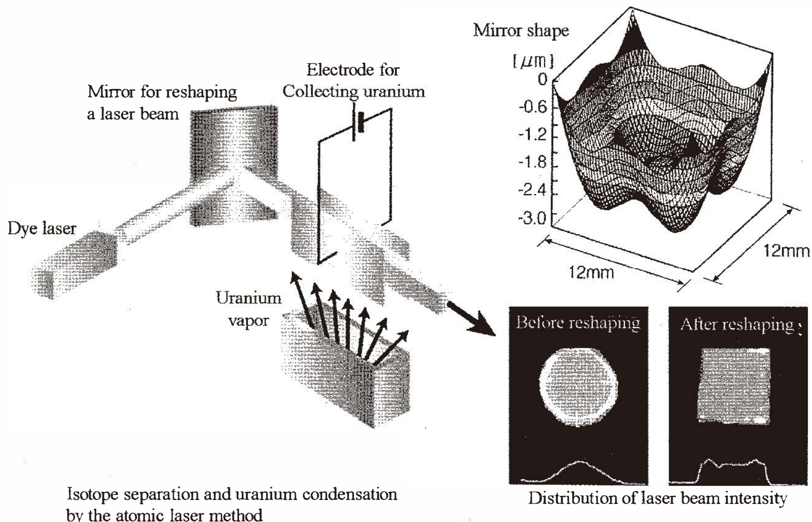



Fig. 17. Laser-beam-reshaping mirror figured by NC P-CVM.

synchrotron radiation. Figure 19 shows a machine suitable for figuring axi-symmetrical objects such as aspherical lenses or SOI wafers. Both machines are installed in a vacuum chamber. After the chamber is evacuated to $10^{-4}$ Torr, it is filled with He gas at atmospheric pressure mixed with reactant gas, and then the NC figuring process is carried out. For all sliding parts such as an XY table, hydrostatic pressure bearings using He gas have been recently adopted. The process gas is circulated through a purifier and heat

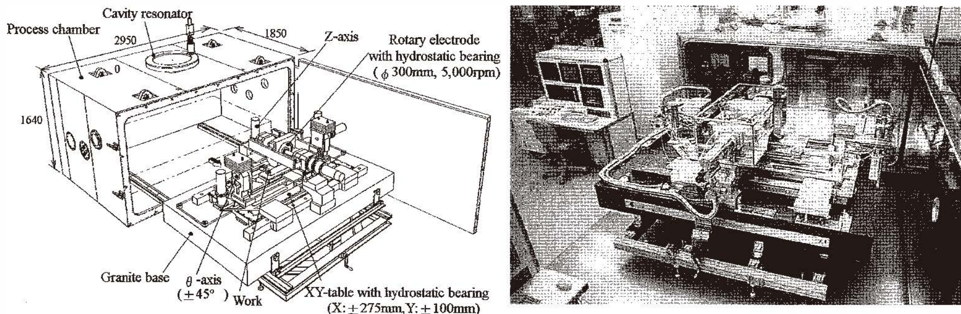



Fig. 18. NC P-CVM machine for X-ray mirror.

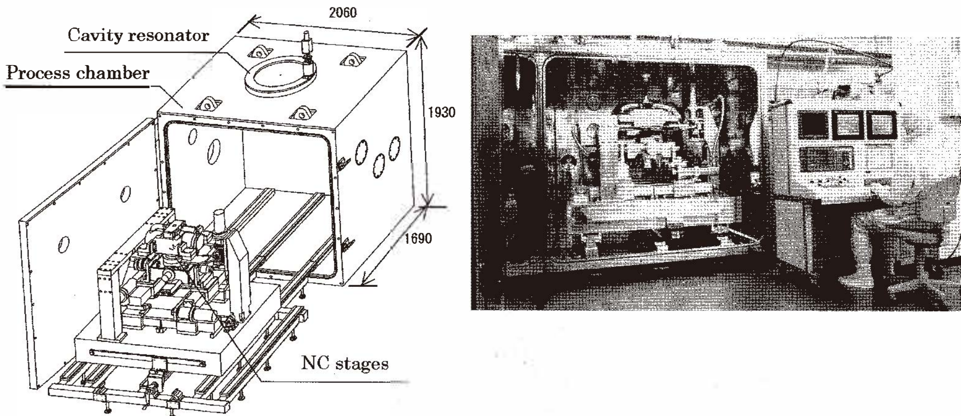



Fig. 19. NC P-CVM machine for axi-symmetrical shape.

exchanger, keeping the purity and temperature. Developing these fundamental technologies, it becomes possible to perform the P-CVM process in an ultraclean environment. If the required machining accuracy or surface roughness cannot be obtained using these P-CVM machines, the finishing process will be carried out by the NC EEM machines shown in Figs. 9 and 10.

### 3.3 *Hydroxyl Electrochemical Machining (H-ECM)*[12–16]

Among the machining processes in which removal of the work proceeds atom by atom are chemical etching and electrochemical machining in the liquid phase. In both methods, surface contamination cannot be avoided, because they utilize solution water mixed with chemicals or electrolyte materials. In LSI processes, where contamination of the processed surface should be completely avoided, the discovery of a new machining or etching method without employing such chemicals will be epoch-making.

The first author started to question the accepted mechanism of electrochemical machining in 1983, and has been considering that electrochemical machining could be made possible only with $OH^-$ ions in pure water without any other chemicals. In the established

theory, the conventional electrochemical machining is understood as follows. As shown in Fig. 20, negative ions of the electrolyte react with the metal surface, and the reaction products are dissolved in water. These products react with water to produce hydroxide ions. Consequently, the concentration of the dissolved electrolyte materials is kept constant.

In contrast, the first author thought of direct interaction of $OH^-$ ions and the metal surface described as follows. Most of the electrolyte materials are alkali metal compounds. Alkali metal ions in the electrolyte solution react with water molecules at the cathode to produce a high density of $OH^-$ ions. $OH^-$ ions are transported to the work surface by the electric field, and then directly interact with the anode metal. To verify the validity of this idea, the following two investigations have been carried out. One experiment was planned to detect the electrochemical removal only by the ultrapure water using the experimental setup shown in Fig. 21. In spite of the very low equilibrium concentration of $OH^-$ and $H^+$

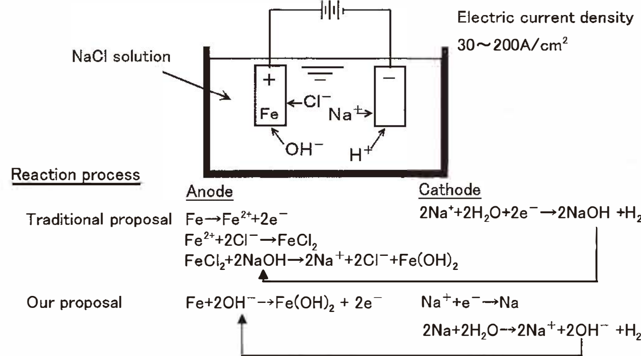
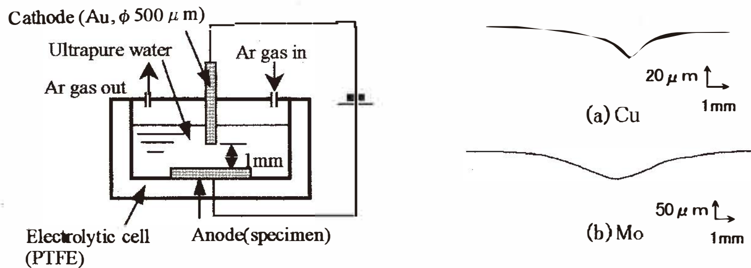



Fig. 20. Elemental process of electrochemical machining using NaCl solution.




**Experimental conditions and results using ultrapure water at room temperature**

| Specimen | Average electric field strength (V/cm) | Obtained electric current density ($A/cm^2$) | Etching time (min) | Results |
|---|---|---|---|---|
| Cu | $1\sim2\times10^6$ | 0.4 | 10 | Etched (Current efficiency: 14%) |
| Mo | $5\times10^5$ | 0.038 | 60 | Etched (Current efficiency: 22%) |
| Fe | $4.5\times10^6$ | 0.016 | 60 | Oxidized |
| Aℓ | $6\times10^6$ | 0.012 | 60 | Oxidized |
| Si | $1\times10^7$ | 0.0079 | 10 | Oxidized |

Fig. 21. Experimental evidence of electrochemical machining of various materials solely by ultrapure water.

ions in the water ($10^{-7}$ mol/l), atomic removal has clearly occurred under a high electric field when Cu and Mo were employed as work materials.

The other investigation was the computer simulation of the elemental reaction process of $OH^-$ and the metal surface based on first-principles molecular-dynamics. At the time the first author started to study H-ECM, the performance of computer hardware and software was insufficient for application on such a large-scale simulation. In the last 10 years the author's group has developed a new algorithm for the simulation software, and it became possible to conduct a large-scale simulation for several tens of hours by using a supercomputer. Figure 22 shows the simulated results of a surface chemical reaction between hydroxyls and the hydrogen-terminated Si (001) surface. It was clarified that the surface Si atom was removed as $SiH_2(OH)_2$ by the attack of two hydroxyls on Si back bonds.

Based on the results of these two investigations, the first author came to believe firmly that electrochemical machining of metal by ultrapure water could be realized. If the catalytic materials to produce $OH^-$ ions by decomposing water molecules are found, electrochemical machining of metals in the ultraclean atmosphere of flowing ultrapure water will be realized as shown in Fig. 23. Thus, the development of the catalytic materials

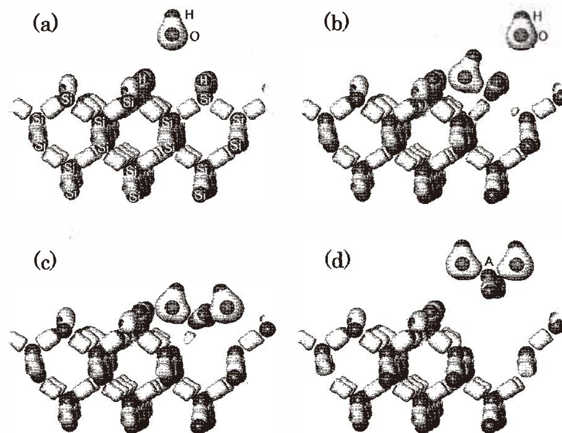



Fig. 22. Chemical reaction between hydrogen-terminated Si(001) surface and hydroxyls (First-principles molecular-dynamics simulation).

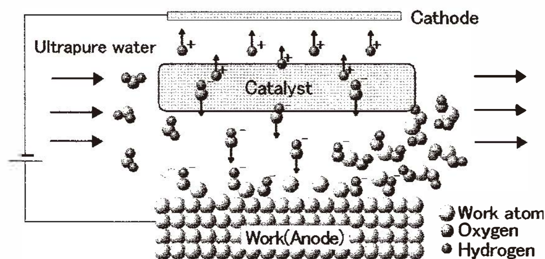



Fig. 23. Electrochemical machining using a catalyst which decomposes the water molecules in ultrapure water.

for decomposing water molecules became very important. Fortunately, the ion-exchange membranes were found to have such catalytic properties. The $OH^-$ concentration obtained was 1000 times higher than $10^{-7}$ mol/ l, that is the $OH^-$ concentration in normal water in the thermodynamically equilibrium state at room temperature. Recently, new catalytic materials have been developed, which have produced $OH^-$ concentration 1,000,000 times higher than normal water at RT as shown in Fig. 24. The first-principles molecular-dynamics simulation has also been quite an efficient tool to develop new catalytic materials.

A result of the H-ECM utilizing newly developed catalytic materials is shown in Fig. 25. Although the ion current density is one order of magnitude lower than that of conventional electrochemical machining, sufficient removal rates for practical use are obtained by the H-ECM in ultrapure water. Construction of a full scale H-ECM machining system has been started.

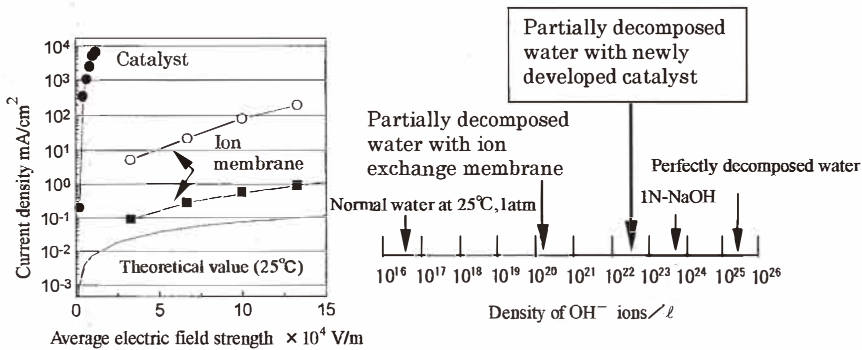



Fig. 24. Relationship between average field strength and obtained electric current density, and the effects of catalyst on water decomposition.

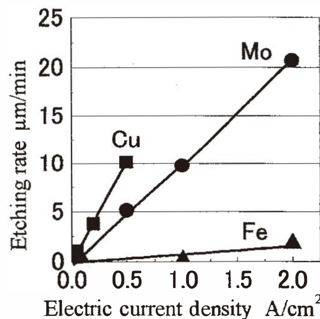



Fig. 25. Relationship between the electric current density and the etching rate for Cu, Mo and Fe anodes.

## 4. Conclusion

This article reviewed research at "Osaka University, Ultra Precision Machining Research Center" and the development of new ultraprecision machining methods. Although many unprecedented research studies are in progress as shown in Fig. 3, it is impossible to describe all of them in this article. Those not addressed at this time will be reported at a later date.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