



Title	Synthesis of Titanium Oxide by Dynamic Ion Beam Mixing(Materials, Metallurgy & Weldability)
Author(s)	Miyake, Shoji; Kobayashi, Takuya; Satou, Mamoru et al.
Citation	Transactions of JWRI. 1989, 18(1), p. 87-91
Version Type	VoR
URL	<a href="https://doi.org/10.18910/4824">https://doi.org/10.18910/4824</a>
rights	
Note	

*The University of Osaka Institutional Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

# Synthesis of Titanium Oxide by Dynamic Ion Beam Mixing†

Shoji MIYAKE\*, Takuya KOBAYASHI\*\*, Mamoru SATOU\*\*\* and Fuminori FUJIMOTO\*\*\*\*

## Abstract

Titanium-oxide thin films were synthesized using dynamic ion beam mixing method. High energy  $O_2^+$  and/or  $O^+$  beams (30 - 40 keV) were injected during the vapour deposition of Ti on Si single crystals and quartz plates. Structure of deposited films revealed that of  $TiO$  in spite of the change of various external parameters. The growth of  $TiO$  crystal had a tendency to vary from (111) to (200) orientation with increase of oxygen ion dose. By the heat treatment of synthesized films at 600°C in the open air the structure changed to include  $TiO_2$ .

**KEY WORDS:** (Ion Beam) (Dynamic Mixing) (Titanium-Oxide) (Thin Film) (Ion Implantation) (Vapour Deposition)

## 1. Introduction

A variety of methods is applied to obtain surfaces with modified structures and properties different from base materials. The one category of the methods are classified to be doping of impurity elements to bulk materials and the other one is synthesis of thin films by the deposition of desired materials. CVD (chemical vapour deposition) and PVD (physical vapour deposition) are typical and well known in the latter category.

In these techniques various ion flows play significant roles, since they are easily controllable in their energy and have a wide variety in their species. Among many ion beam processes for surface modification such as ion implantation, ion beam sputtering, ion plating, ion beam deposition, ion beam mixing, ion and vapour deposition (dynamic ion beam mixing), the dynamic mixing method has a unique character<sup>1)</sup> in the process technique.

In this method the interface between deposited layer and substrate is mixed by high energy ions and much stronger sticking is guaranteed than in other deposition techniques. While in the improvement of wear resistance, ion implantation is attractive and applied to various elements. The thickness of the modified layer, however, is usually very small in this method and a long time operation of the coated element is rather difficult. In the dynamic mixing a modified layer having a necessary thickness is easily obtained with a high wear resistance. Furthermore by changing ion dose and vapour deposition rates, the inclusion of each component within the layer can be controlled comfortably.

Experimental studies on thin film formation by dynamic ion mixing have been devoted to synthesis of nitrides<sup>2-4)</sup> and carbonized materials<sup>5)</sup>. In the formation of TiN film on Si substrates an interesting feature was found<sup>3)</sup> that the crystal growth of TiN developed in the direction of the incident  $N_2^+$  beam, whose reason is not clear at present. In the study of BN formation<sup>4)</sup> structure of c-BN has been verified including h-BN layer.

As for oxide films no experiment has been reported in the dynamic mixing. We were interested in obtaining titanium oxides for the application to optical and/or electrical coating film. We also aimed at examining the orientation of the crystal growth which was found in the case of TiN formation. In this report the first experimental results on the synthesis of titanium oxides by dynamic ion beam mixing are described.

## 2. Experimental Procedures

Figure 1 shows schematic diagram of experimental apparatus. The apparatus is composed of ion source, acceleration and analyzing system and reaction chamber. Ions are extracted from a cold cathode type PIG ion source, accelerated and magnetically mass analyzed as desired ion species. The  $O_2^+$ - or  $O^+$ -beam is irradiated from below on to a substrate about 40 cm apart. The ion beam current to the substrate is measured by a current integrator. The SUS reaction chamber has a dimension of about 50 cm inner-diameter and about 40 cm height, within which a substrate holder and an EB evaporator are installed. Quantity of evaporated materials is measured by

† Received on May 8, 1989

\* Associate Professor

\*\* Graduate Student

\*\*\* Chief Researcher, Government Industrial Research Institute

\*\*\*\* Professor, Institute of Scientific and Industrial Research, Osaka University

Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

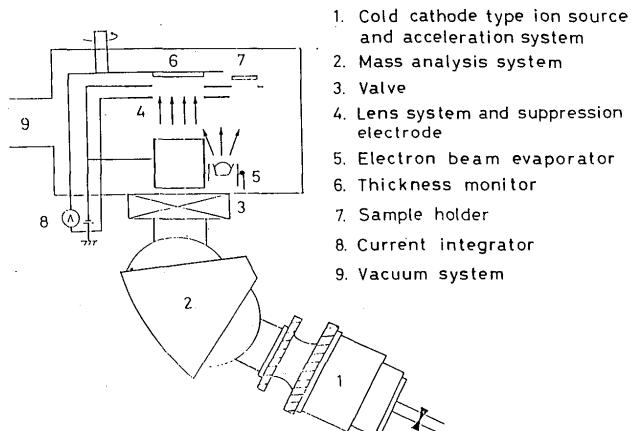


Fig. 1 Schematic diagram of experimental apparatus.

a thickness monitor set at the same height with the substrate, towards which ion beams and evaporated atoms and/or molecules propagate nearly in parallel each other. The chamber is evacuated with a TM pump to a base pressure of  $3 \times 10^{-4}$  Pa, which does not change appreciably even during the film synthesis due to the gettering action of Ti.

The maximum acceleration voltage of ions was 40kV in which the maximum beam current of  $O_2^+$  was  $200\mu A$ . At 30kV operation the current was  $15\mu A$  and in the case of  $O^+$  beam of 40kV the current obtained was  $70\mu A$ . The operating condition of the EB evaporator was typically 4kV acceleration with 40–60mA in the EB current.

In the measurement of synthesized film thickness a Talystep was used having the maximum magnification of  $10^6$ . To clarify structure and composition of the films, XRD (X-ray diffraction), RBS (Rutherford backscattering) and Raman scattering analysis were performed. The optical property was examined from visible-UV absorption characteristics.

Substrates used for the synthesis are Si(111) and Si(100) single crystals as well as quartz plates. Thickness of synthesized films were typically 1000A and 3000A. The former was applied for RBS and visible-UV absorption analysis. Ion dose corresponding to the formation of a film of 3000A thickness was about  $4 \times 10^{18}$  at a Ti/O ratio of 1 and it gave a dose rate of  $4 \times 10^{17}$  dose/cm<sup>2</sup>. The substrate temperature during synthesis was below 200C at most. After deposition specimen were heat-treated in the open air at 300C and 600C.

### 3. Results and Discussion

#### 3.1 Outlook of synthesized film

Outlook of the films synthesized is colored brown and transparent on a Si wafer. While it has a metallic luster on a glass plate. The surface is hard enough not to be scratched by a knife edge. By the heat treatment of films at 300C

for 2 hours there appeared no variation, but by the heating at 600C the surface color changed from transparent brown to transparent green or red within 30 minutes from the treatment. It is similar to the color of  $TiO_2$  obtained by vapour deposition only on a Si substrate. In the case of a film formed on a glass plate the outlook became transparent after 30 minutes from the treatment.

#### 3.2 Measurement of film thickness

Figure 2 shows a dependence of the ratio  $Th_{me}/Th_{ev}$  on the ratio of the number of  $O_2^+$  and Ti particles, where  $Th_{me}$  is the thickness measured by the Talystep and  $Th_{ev}$  is that by the thickness monitor during evaporation of Ti. From this data the sputtering rate of Ti against  $O_2^+$  irradiation can be estimated, and it shows nearly a constant value in spite of an increase in  $O_2^+$  dose. Sputtering yield of  $O^+$  ions injected into Ti plate is estimated<sup>6)</sup> to be 0.53–0.58 for the ion energy of 15–20keV per atom. In the case of  $O_2^+$  ion irradiation of 40keV the ion energy per atom is 20keV and the yield is calculated to be a value of 0.53. It indicates that when a Ti film with a thickness of 1000A is sputtered by  $O_2^+$  ions the thickness is reduced to about 470A. Actually, however, it is about 650A as shown in Fig. 2. It can be assumed that in the dynamic mixing a peculiar process would occur which is different from usual ion implantation, since vapour deposition and ion implantation simultaneously progress during the synthesis. Sputtering process during dynamic mixing is very complex and quite little studies have been reported.

#### 3.3 XRD analysis

In Fig. 3 typical XRD chart is given in the case of

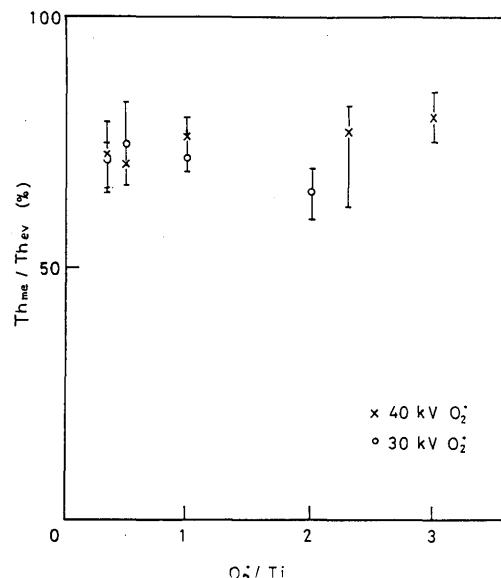


Fig. 2 Dependence of  $Th_{me}/Th_{ev}$  on  $O_2^+/Ti$ .

40 keV ion energy for different ratios of the number of Ti atoms and  $O_2^+$  ions. From analysis of the data by A.S.T.M. cards we find clear evidence of  $TiO$  formation with peaks at  $42^\circ$ ,  $60^\circ$ , and  $36^\circ$ . Other peaks include those of Si and Ti. It is clear that with an increase of titanium atoms against oxygen ions the film structure changes from  $TiO$  single-phase to  $TiO + Ti$  double-phase.

It is well known that titanium oxides fabricated by various methods<sup>7-13</sup> have a structure of anatase- and rutile-type  $TiO_2$ . Formation of  $TiO$  is reported<sup>10</sup> only in a limited condition in an experiment of ion implantation, where the film has a structure of monoclinic crystal. While in our experiment an NaCl-type tetragonal crystal is synthesized. It is interesting that formation of  $TiO$  is found when injected ion energy is very large. In both dynamic mixing and ion implantation it can be assumed that ions would transfer their directional energy to thermal one when they collide with the substrate, by which a local high temperature region is produced with a rapid cooling process. We consider this feature would result in the formation of  $TiO$  characteristic of dynamic mixing and/or ion implantation.

The peak intensity ratio of  $TiO(111)$  and  $TiO(200)$

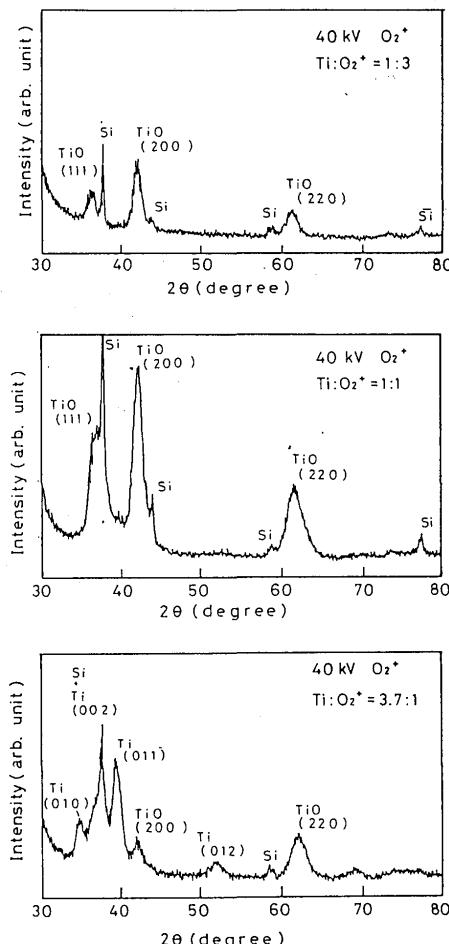


Fig. 3 XRD chart of films for different  $Ti/O_2^+$  ratios.

observed in XRD is plotted in Fig. 4 as a function of  $Ti/O_2^+$  ratio of the number of Ti atoms to that of  $O_2^+$  ions. The peak intensity ratio clearly increases with  $Ti/O_2^+$ . This result is similar to the one reported<sup>3</sup> in the case of  $TiN$  formation and is very interesting in the point that even when the ion species is different a common mechanism of film growth will govern in the dynamic mixing due to the simultaneous mixing process of deposited vapour and implanted ions.

The structure of  $TiO$  is known to be a rock-salt type. When the injected  $O_2^+$  dose is small, the film is apt to grow in the (111) direction which is more stable in the energy state of the crystal. As the ion dose is increased, the radiation damage to the crystal growing in the (111) direction becomes remarkable and a growth to a different (200) direction will result which is not dense looking from the direction of ion irradiation.

We obtained XRD data by changing acceleration energy and species of injected ions, whose result is shown in Fig. 5. It is clear that formation of  $TiO$  not of  $TiO_2$  is again verified in the figure even when external parameters

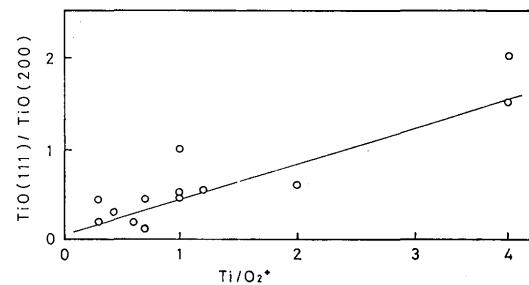


Fig. 4 Peak intensity ratio of  $TiO(111)$  and  $TiO(200)$  observed in XRD chart versus  $Ti/O_2^+$  ratio

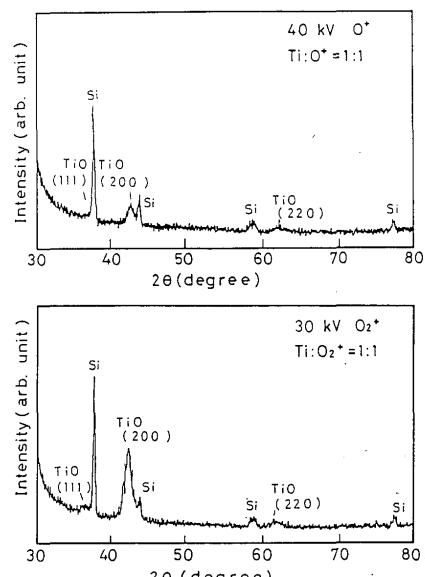


Fig. 5 XRD chart of films for different external parameters.

are varied. The peak intensities corresponding to  $\text{TiO}$  are rather weak in comparison with the case in Fig. 3. This is mainly due to the smaller  $\text{O}^+$  ion current of  $75\mu\text{A}$  at  $40\text{kV}$  and  $\text{O}_2^+$  current of  $15\mu\text{A}$  at  $30\text{kV}$ , whereas  $\text{O}_2^+$  current of about  $200\mu\text{A}$  at  $40\text{kV}$  in the case of Fig. 3.

The lattice constant of NaCl-type  $\text{TiO}$  according to A.S.T.M. card gives a value of  $4.29$ , while the constant estimated from XRD data is evaluated to be in the range of  $4.07\text{--}4.42$ .

Figure 6 shows XRD charts after heat treatment at  $600\text{C}$  of the specimen in the case of  $40\text{kV} \text{O}_2^+$  beam with  $\text{Ti}/\text{O}_2^+ = 1$ . There appears a little variation of the spectra by changing the treatment time from  $0.5$  to  $6.0$  hours. The peak intensity of  $\text{TiO}$  spectra diminishes, while peaks of  $\text{TiO}_2$  around the diffraction angles of  $36^\circ$ ,  $54^\circ$ , and  $69^\circ$  grow with the treatment time. It should be noticed that even after  $6$  hours' treatment the film still has a structure of  $\text{TiO} + \text{TiO}_2$  double phase. While in the treatment at  $300\text{C}$  the XRD chart did not show any change even after  $2$  hours' operation. From differential thermal analysis it is found<sup>14)</sup> that the transformation of titania from  $\text{TiO}$  to  $\text{TiO}_2$  is induced at  $480\text{C}$ , which is consistent with our

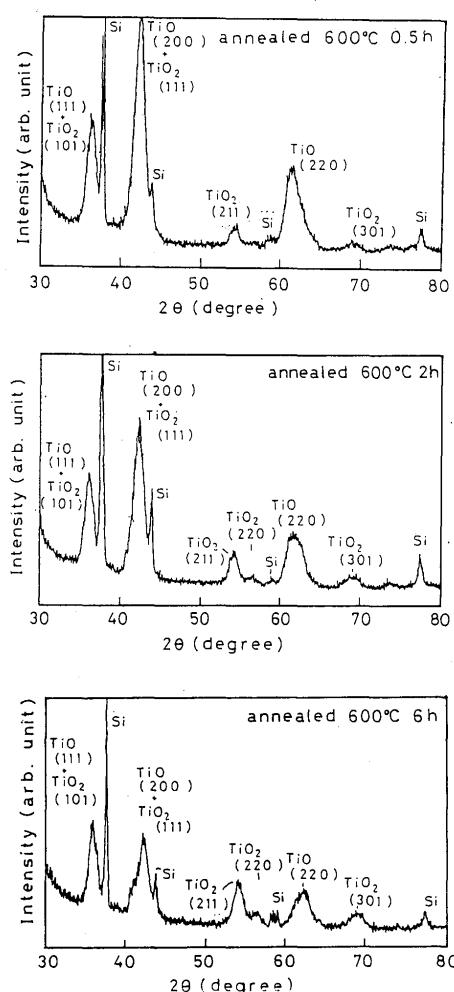


Fig. 6 XRD chart of films after heat treatment.

result of observing the appearance of  $\text{TiO}_2$  in the  $\text{TiO}$  structure at  $600\text{C}$ , not at  $300\text{C}$ .

### 3-4 RBS analysis

Typical RBS spectrum of the synthesized film is shown in Fig. 7. In the figure the spectrum of Ti has an asymmetric profile with a gentle slope on the left side. It is a clear appearance of the mixing process of Ti on the interface with the Si substrate. From RBS data we evaluated the ratio of the number density of Ti and O atoms and plotted it as a function of  $\text{Ti}/\text{O}_2^+$  in Fig. 8. In the figure it is found that the ratio of Ti/O keeps nearly a constant value of about  $0.55$  up to about  $2$  of  $\text{Ti}/\text{O}_2^+$ , above which it increases to about  $1.0$  because of the increase of Ti phase within the film.

It is generally known<sup>15)</sup> that  $\text{TiO}$  has a structure with many vacancies and the stoichiometric composition rate is widely spread between  $\text{TiO}_{0.6}$ – $\text{TiO}_{1.25}$ . Our data in Fig. 8, however, seems to indicate that about  $50\%$  of Ti lattice points are vacant or defects in titanium lattice develops more than  $50\%$  accompanied by those of oxygen, which is quite peculiar. To verify this interpretation a further experiments are necessary as well as the problem of the epitaxial crystal growth observed in Fig. 4.

### 3.5 Visible-UV absorption

Figure 9 shows absorption characteristics of synthesized films in the range of  $300\text{--}600\text{nm}$ . In the figure three data are given where the one designated by "no an-

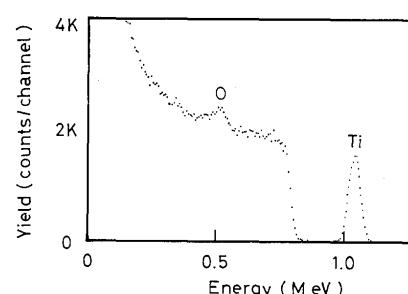


Fig. 7 RBS spectrum of synthesized film

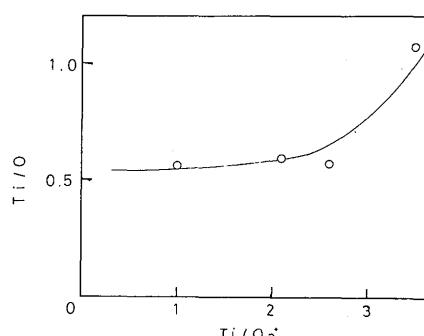


Fig. 8 Ratio of Ti and O atoms estimated from RBS data versus  $\text{Ti}/\text{O}_2^+$  ratio.

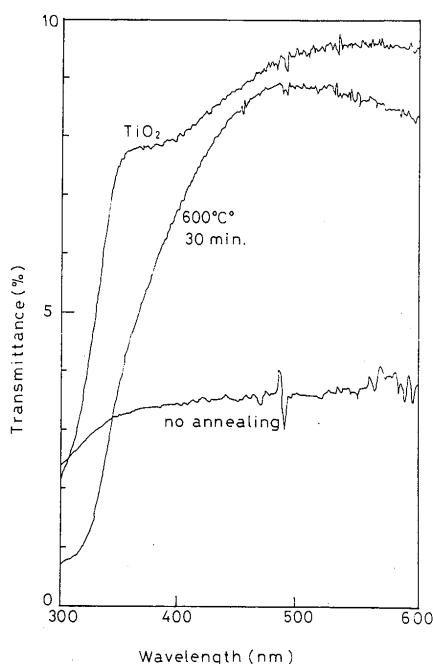


Fig. 9 Visible UV absorption characteristics of films with and without heat treatment.

nealing" is that of as-deposited film of  $\text{TiO}$  by the mixing and the curve of "600C, 30min." corresponds to the heat-treated film at 600C for 30 minutes revealing  $\text{TiO} + \text{TiO}_2$  structure. While the curve of "TiO<sub>2</sub>" is that of TiO<sub>2</sub> obtained by the simple vapour deposition method. With no annealing almost flat characteristics is observed which will reflect the property of  $\text{TiO}$ . By the heat treatment the curve rereveals a property similar to that of TiO<sub>2</sub>. This is consistent with the result by XRD given in Fig. 6.

As for Raman scattering we could not obtain a clear evidence of the formation of  $\text{TiO}$  and/or TiO<sub>2</sub> partly due to the very small film thickness.

#### 4. Conclusion

Using the dynamic ion beam mixing method titanium oxide films were fabricated on Si single crystals. Ion acceleration energy, ion species and quantity of evaporated titanium were varied as external parameters. Structure and composition of synthesized films were characterized by XRD, RBS, Raman scattering and visible-UV absorption. Following results were clarified experimentally.

- 1) As-deposited films were all  $\text{TiO}$  and not TiO<sub>2</sub> irrespective of the variation of external parameters.
- 2) The crystal growth of  $\text{TiO}$  changed from (111) to (200) direction when the number of oxygen ions against Ti atoms was increased.
- 3) The structure of  $\text{TiO}$  synthesized had a ratio of about

0.5 in the composition of Ti to O atoms until the number of evaporated Ti atoms is twice that of O<sub>2</sub><sup>+</sup> ions.

- 4) By the heat treatment of the film at 300C there appeared no change in the XRD spectra as well as in the outlook. While at 600C treatment TiO<sub>2</sub> spectra was obtained in addition to  $\text{TiO}$  and a variation of the colour of the film from brown transparent to green or red transparent was observed, which was typical of TiO<sub>2</sub> film fabricated by various methods.
- 5) Visible-UV absorption characteristics of as-deposited film had almost flat characteristics in the range of 300–600 nm. By the heat treatment at 600C it changed to a character similar to that of TiO<sub>2</sub> fabricated by the simple vapour deposition. This result is consistent with that of XRD.

#### Acknowledgements

The authors would like to express their gratitude to Drs. M. Kiuchi, A. Chayahara and K. Fujii of Government Industrial Research Institute, at which experiments were performed, for their support and critical comments to this study. They also thank to Mr. Y. Sakura and Mr. T. Kan for their help in the experiment, to Dr. N. Umesaki for his help in the Raman scattering analysis and to Dr. Y. Makino for his interest and comments to this work.

#### References

- 1) M. Satou, S. Fukui and F. Fujimoto: *Proc. 5th Symp. Ion Source and Ion-Assisted Technology*, (Tokyo, 1981) p. 349.
- 2) M. Satou, K. Yamaguchi, Y. Andoh, Y. Suzuki, K. Matsuda and F. Fujimoto: *Nucl. Instrum. & Methods* **B7/8** (1985) 910.
- 3) M. Kiuchi, K. Fujii, T. Tanaka, M. Satou and F. Fujimoto: *Nucl. Instrum. & Methods* **B33** (1988) 649.
- 4) M. Satou and F. Fujimoto: *Jpn. J. Appl. Phys.* **22** (1983) L171.
- 5) C. Weismantel: *J. Vac. Sci. & Technol.* **A3** (1985) 2384.
- 6) N. Matsunami, Y. Yamamura, Y. Itikawa, N. Itoh, Y. Kazumata, S. Miyagawa, K. Morita, R. Sfumizu and H. Tawara: *IPPP-AM-32*, (IPPF, Nagoya Univ., Nagoya, 1983)
- 7) V.P. Rozhnov, G.S. Cheremukhin and A.M. Klochov: *Sov. J. Opt. Technol.* **45** (1978) 652.
- 8) H. Demiryont and J.R. Sites: *J. Vac. Sci. & Technol.* **A2** (1984) 1457.
- 9) J. G. Perkins: *Thin Solid Films* **9** (1972) 257.
- 10) Y. Okabe, M. Iwaki and K. Takahashi: *Kizoku Hyoumen Gijutsu* **39** (1988) 656 (in Japanese).
- 11) H. Matsuami: *Kougyou Zairyou* **36** (1988) 43 (in Japanese).
- 12) K. Fukushima and I. Yamada: *J. Appl. Phys.* **65** (1989) 619.
- 13) H. Komiyama: *Seramikkusu* **21** (1986) 305 (in Japanese).
- 14) S. Kobayashi, D. Shibata, K. Yajima and F. Suzuki: *Kougyou Zairyou* **32** (1984) 50 (in Japanese).
- 15) O.T. Sorensen: *Nonstoichiometric Oxides* (Academic Press, 1981) p. 198.