

Low Temperature Crystallization of TiO₂ Films by Sputter Deposition

Yasunori Taga and Naoomi Yamada

Abstract: Crystalline TiO₂ film was formed on PET(polyethylene terephthalate) film by radio frequency sputter deposition method using a sintered TiO₂ target by adding H₂O gas to Ar gas for sputtering. X-ray diffraction analysis revealed that the crystal structure of the film of 100 nm thick was confirmed to be anatase crystallites of TiO₂. In order to elucidate the mechanism of low temperature crystallization thus observed, direct measurement of surface temperature of growing films during sputter deposition was carried out by two methods of an infrared thermometer from the outside of vacuum chamber and a thermocouple attached to the growing film surface. Upon the beginning of sputter deposition in Ar gas, film temperature increased rapidly and became constant at 120 °C after 30 min. Addition of H₂O gas to Ar gas for sputtering resulted in further increase in film temperature and reached to 230 °C depending on the deposition conditions. Furthermore, photocatalytic performance of decomposition of methylene blue was examined to be enhanced remarkably as a result of crystallization of the film. It was concluded that low temperature crystallization of TiO₂ film by sputter deposition was explained in terms of local heating of thin shallow surface region of growing film by kinetic energy deposition of sputtered particles.

Keywords: *Sputter deposition, Low temperature crystallization, TiO₂, Kinetic energy, Sputtered particles, Surface diffusion, Reconstruction, Crystallite*

1. Introduction

Thin film deposition by sputtering at low temperature has lately attracted much attention from the viewpoints of thin film formation on organic substrates, fabrics and plastic films for application to energy harvesting and storage. ^{[1]~[4]}

Sputtered films at low temperature, however, sometimes showed insufficient properties such as density, refractive index, crystallinity, and adhesion to substrate. Post annealing up to 150 °C to 200 °C after deposition is therefore necessary to obtain durability to practical application. One of the most essential problems is to measure the real temperature of thin film during growth by sputter deposition. According to the recent report by Musil et al.^[5], the substrate temperature during sputter deposition of TiO₂ by thermostrips pasted to glass substrate and reported a big difference in temperature between substrate and holder depending on various deposition conditions. They reported that the temperature was 160 °C for unheated glass substrate and anatase structure was observed only for the films thicker than 1000 nm. Pasting of thermostrips on substrate surface, however, may give influence to some extent on the temperature of the growing films. This influence will be

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prominent especially for thinner films less than a few hundred nm thick.

This manuscript describes at first the results of direct measurement of surface temperature of growing TiO₂ films during sputter deposition by the sophisticated two different techniques: One is an infrared thermometer from the outside of vacuum chamber without touching on the film surface and the other a thin film thermocouple attached to the growing film. The crystal structure of the film at 100 nm thick thus prepared was confirmed by X-ray diffraction and photocatalytic performance of the crystallites TiO₂ film was examined by the photodecomposition of methylene blue.

2. Experimental procedure

The thin film temperature was measured by two different methods such as a thin film temperature sensor (Pt-100, METSUSHIN) attached to the front and back of substrate and an infrared thermometer (IT-550, HORIBA) via BaF₂ window from the outside of the chamber. Therefore, substrate temperature measured in this study denoted a real growing film temperature after calibration by taking the emissivity of the film into consideration. TiO₂ films were deposited on nonalkali glass substrates(#1737, CORNING, 50mm x 50mm) by RF(radio frequency) magnetron sputtering using a sintered TiO₂ target (99.9% KOJYUNDO CHEMICAL LABORATORY). Deposition chamber was first evacuated to 5×10^{-5} Pa and then sputtering gas of Ar and H₂O was introduced to the pressure range of 0.4 to 10.0 Pa by controlling the water vapor pressure by the system to adjust the partial pressure ratio $K(= P_{H_2O} / P_{Ar+H_2O})$ of Ar and H₂O as shown figure 1. The system to control and monitor the gas composition during sputtering was equipped with a quadruple mass analyzer in supplementary chamber attached to the deposition chamber using differential pumping system with a small nozzle and skimmer. By using this system, the partial pressure of Ar and H₂O gases was successively measured during sputter deposition. Sputter deposition of TiO₂ films was carried out under the following conditions: input power for a sintered TiO₂ target of 76.2 mm in diameter was 400 W, the sputtering gas pressure was in the range of 0.4 to 10.0 Pa and a target to substrate distance was kept constant at 10 cm throughout this study. The structure of the film was examined by X-ray diffraction (XRD) analysis using Cu-K α_1 radiation. Atomic force microscope (AFM) was used to determine film thickness and observation of surface morphology.

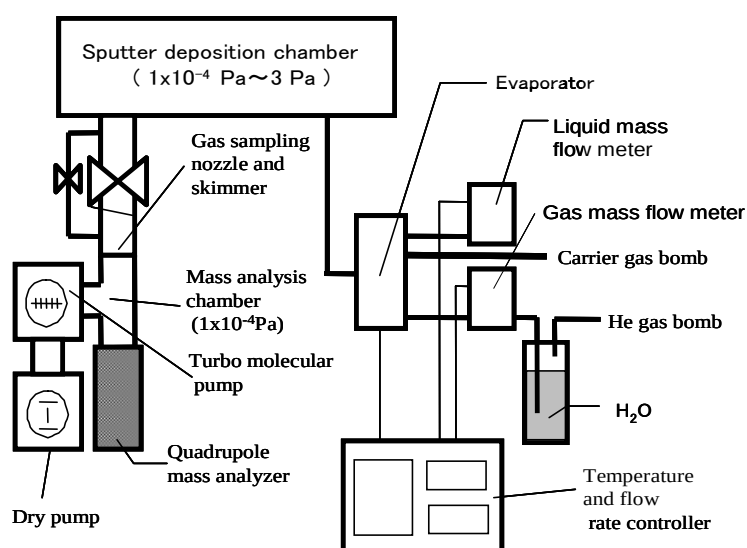


Fig.1 Schematic representation of sputter deposition chamber with gas introduction and monitor system

3. Results and discussion

Changes in temperature of the front and back surfaces of the substrate during sputter deposition in Ar gas were first measured by temperature sensors. The film temperature rapidly increased and reached to 120 °C after 10 min of deposition, where temperature difference between the front and back surfaces was confirmed to be 27°C under the present experimental conditions. In addition, temperature measured by infrared thermometer showed a good coincidence with that of the front surface by temperature sensor. Based on these results, the film temperature in this study hereafter denotes surface temperature of the growing film measured by infrared thermometer during deposition.

Figure 2 shows the changes in the film temperature and deposition rate with time under the sputter gas composition of Ar and H₂O as a parameter. Film temperature increased rapidly and reached to 120 °C during sputtering in Ar gas. Upon introduction of H₂O gas in Ar to partial pressure P_{H_2O} to 5×10^{-1} Pa, film temperature began to increase again and finally saturated at 230 °C. Present study revealed that film temperature during sputtering in mixed gas of Ar and H₂O increased to unexpectedly high at about 230 °C under the present experimental conditions. However, it can be also possible to deposit TiO₂ films on organic substrate such as PET (polyethylene terephthalate) without melting or damage of deformation under the above conditions. These results can be explained in terms of local heating of the growing film during sputter deposition occurred only in a very shallow surface region of the film. It was generally understood that the film surface during growth by sputter deposition received a large amount of energy deposited from impinging sputtered particles such as Ti and O, ionized gas molecules and electrons in glow discharge plasma for sputtering^{[6]~[9]} and as a result, film temperature rose with the deposition time elapsed. Among these factors, introduced O₂ gas or decomposed O₂ from introduced H₂O may play an important role on the substrate temperature. Actually, O₂ gases in the deposition chamber may arise from introduced gas for sputtering and sputtered atoms and molecules from TiO₂ target. O₂ gases thus existing in the chamber may decompose or ionize in plasma into various forms such as O, O⁺, O⁻, O₂⁺, O₂⁻, but it is difficult to identify what is the dominant form of O₂ gas in the present plasma conditions^{[10],[11]}. However, O atoms are known to have a tendency to be ionized in electronegative state such as O⁻ and O₂⁻ which will be accelerated to the substrate by the potential difference of several hundred electron volts between target and substrate. Deposition and accumulation of the kinetic energy of impinging oxygen related ions may result in local heating of the shallow region of the growing films.

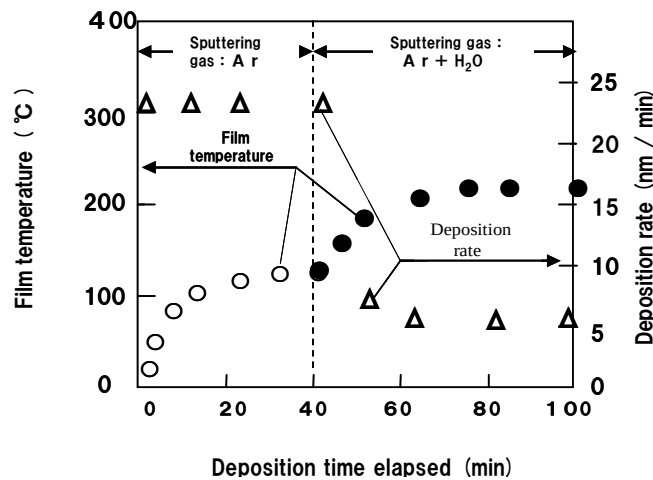


Fig.2 Changes in film temperature and deposition rate with time as a function of sputtering gas composition.

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The film temperature will be decided as a result of balance between deposition energy and the diffusion of deposited heat in the film to the substrate. On the other hand, deposition rate of the film rapidly decrease by adding of O₂ or H₂O gas in Ar.

Target surface sputtered by Ar ions may result in oxygen deficiency state such as be TiO_{2-x} due to selective sputtering of Ti and O which weakened the surface binding energy to enhance the sputtering yields⁹⁾.

Figure 3 showed the changes in XRD spectra of the films as a function of partial pressure ratio $K = P_{\text{H}_2\text{O}} / P_{\text{Ar}+\text{H}_2\text{O}}$ in gas mixture. It can be seen clearly from the figure, crystalline structure containing small anatase crystallites TiO₂ was first found at partial pressure ratio $K = 0.55$. Local temperature enhancement of the growing film was caused by adding H₂O gas in Ar during sputtering. In order to confirm the effect of film temperature on the crystallization of TiO₂ films, more detailed experiment to deposit TiO₂ films below 100 °C was carried out by intermittent sputter deposition, i.e. the film was deposited by repeating of 10 min deposition and 10 min pause to keep film temperature below 100 °C. X-ray diffraction analysis of TiO₂ films thus deposited under film temperature below 100 °C revealed to be amorphous. These results can be understood that TiO₂ films sputtered under mixture gas of Ar and H₂O gases partially crystallized as a result of increase in film temperature by local energy deposition by negative oxygen ion bombardment.

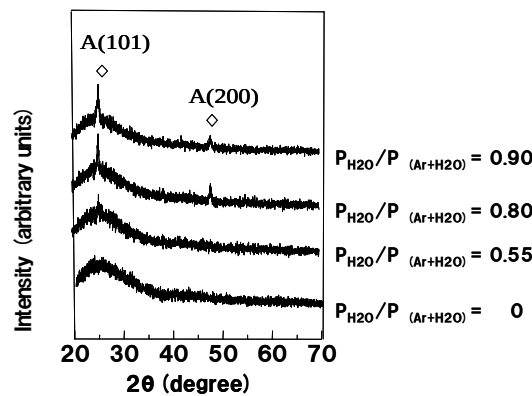


Fig.3 Changes in XRD spectra of TiO₂ films as a function of partial pressure ratio K.

Film thus obtained may have a structure containing small anatase crystallites TiO₂ in amorphous TiO₂ matrix.

Effects of introduction of O₂ or H₂O gas in Ar on the growth of crystallites in TiO₂ films were also confirmed by post annealing of the films deposited at 120 °C using Ar gas. Figure 4 showed that as deposited TiO₂ films showing amorphous structure became crystallized after annealing at 400°C. Introduction of O₂ or H₂O gas in Ar resulted in the growth of crystallites in TiO₂ at 230 °C and the post annealing of the film deposited at 120 °C also gave rise to the growth of crystallites at 400°C. These differences in temperature for crystallization may be explained in terms of physical and chemical effects on the growing film surface such as negative ion bombardment and the exothermal enthalpy change on the films surface as a result of chemical reaction between H₂O molecules and particles approaching to the surface such as Ti atoms or molecules^[12].

Introduction of H₂O gas during sputtering was reported in several papers in order to prepare transparent conductive oxide (TCO) films^{[13]~[16]}. Recently, Koida et al. formed hydrogen-doped In₂O₃ films in sputtering gas of Ar with partial pressure of H₂O from 1x10⁻⁵ Pa to 1x10⁻² Pa and reported that introduction of water vapor suppressed the growth of crystallites. On the contrary, the present results showed the introduction of H₂O gas in Ar accelerated the growth of crystallites in TiO₂ as a result of local heating of the shallow region of the growing film. It may be impossible to compare the present results with that of Koida et al. quantitatively because of large experimental conditions such as target materials and P_{H₂O}. Because of the restriction

of the present experimental system, TiO_2 film growth under K values smaller than 0.55 was impossible. Actually, the film deposited in Ar gas which corresponds to K value of 0.01 showed an amorphous structure in the present study.

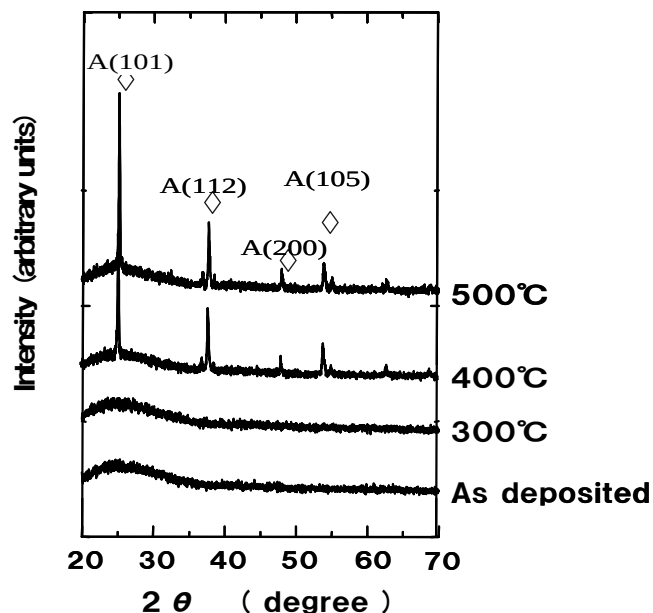


Fig.4 Changes in XRD spectra of TiO_2 film as a result of post annealing temperature.

4. Conclusion

growing film temperature depending on the growth conditions, where the maximum film temperature Introduction of H_2O gas in Ar during sputter deposition resulted in remarkable enhancement of was 230 °C. The crystallites of anatase TiO_2 in the films was formed for partial pressure ratio K over 0.55. These results can be explained in terms of local heating of thin shallow surface region of growing film by kinetic energy deposition of sputtered particles and oxygen negative ion bombardment.

References

- 1) M. Takeuchi, T. Yamasaki, K. Tsujimaru, and M. Anpo: Chemistry Letters 35, 904 (2006).
- 2) Y. Kurokawa, T. Segawa, T. Miyamoto: Eng.Rep. 52, 31 (2002).
- 3) R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga: Science 293, 269(2001).
- 4) Y. Taga, Thin Solid Films 517, 3167(2009).
- 5) C.J. Tavares, S.M. Marques, T.Viseu, V. Teixeira, J.O. Camerio, E. Alves, N.P. Barradas, F. Munnik, T. Girardeau, and J.P. Riviere J. Appl. Phys. 106, 113535(2009).
- 6) J. Musil, D. Herman, and J. Sicha: J. Vac. Sci. Technol. A4, 521 (2006).
- 7) D. J. Kester and Russell Messier: J. Vac. Sci. Technol. A4, 496(1986).
- 8) Y. Taga: MRS Proc. 268, 95(1992).
- 9) P. Sigmund: Phys. Rev. 184, 383(1969).
- 10) M. W. Thompson: Philos. Mag. 18, 377(1968).
- 11) T. Ohwaki and Y. Taga: Appl.Phys. Lett. 54, 1164 (1989).
- 12) T. Ohwaki and Y. Taga: Appl. Phys. Lett. 59, 420(1991).
- 13) T. Kawaharamura: Privatre communication.

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- 14) S. Ishibashi, Y. Higuchi, Y. Ota, and K. Nakamura, J. Vac. Sci. Technol. A8, 1399 (1990).
- 15) M. Ando, M. Takabatake, E. Nishimura, F. Lenlanc, K. Onisawa, and T. Minemura: J. Non-Cryst. Solids 28, 198 (1996).
- 16) T. Koida, H. Fujiwara and M.Kondo: Jpn. J. Appl. Phys. 46, L685 (2007).