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High Rate Deposition of TiO_2 Thin Films using Pulse Sputtering Technique

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Abstract High rate deposition of TiO_2 thin films is attempted using a pulse sputtering technique with oxide target. Compared with the conventional dc technique, sputtering can be performed stably at a high input power. A deposition rate above 1 nm/sec is easily achieved, although the deposition rate depends strongly on the oxygen gas content of the sputtering gas. The increase in deposition rate, however, leads to a decrease in the refractive index and an increase in transparency, which suggests that the film deposited at a high deposition rate has a porous structure. On the other hand, an increase in oxygen gas content in the sputtering gas leads to crystallization in the film. This results in an increase in the refractive index as large as 2.5 at a 500 nm wave length.

Key words: TiO_2, pulse sputtering, high rate deposition, oxide target, low temperature deposition

1. INTRODUCTION

TiO_2 thin film is a very useful optical material with a high refractive index. Recently, many researchers have shown an interest in the photocatalysis properties of TiO_2 film. For this, the development of thin film production techniques for TiO_2 is one of the key technologies. Up to now various kinds of thin film deposition techniques have been used to obtain TiO_2 thin films [1-3]. Pulse sputtering appears to be a useful technique for the deposition of the film, since it can stably deposit insulating oxide thin films at a high rate [4-6]. In this work, high rate deposition of TiO_2 thin films using a pulse sputtering technique with a titanium oxide target was attempted. A deposition rate above 1 nm/sec was easily achieved with the system, although the deposition rate strongly depended on the oxygen gas pressure. The increase in deposition rate, however, led to a decrease in the refractive index. This seemed to be caused by the formation of films with a porous structure.

In this paper, preparation conditions, and structure and optical properties of the films deposited by the pulse sputtering technique are reported in detail.

2. EXPERIMENTAL

A conventional magnetron sputtering system with 10 cm diameter sputtering source was used to deposit TiO_2 films. Deoxidized titanium oxide target, made by Furuya Metal Co., was used in the film preparation. Sputtering was performed in an $Ar+O_2$ mixture. A pulse electric source of 20 kHz to 100 kHz was used and sputtering was performed at various pulse voltages, pulse widths and pulse frequencies. Films with thicknesses of about 200 nm were deposited on the glass slide substrate. Typical film preparation conditions are listed in Table 1.

Film thickness was measured with a surface profile measuring system, Decktak 3030. The structure and surface morphology of the prepared films were evaluated using x-ray diffractometry and atomic force microscopy (AFM). The optical properties of the films, such as transmittance, refractive index at 500 nm, and optical band gap were evaluated using an optical spectrophotometer.

Table 1. Typical film preparation conditions.

Target	10 cm ϕ TiO_{2-X} disk
Sputtering gas	Ar + 0~30% O_2 mixture
Gas pressure	2 mTorr
Pulse voltage	500 V ~ 1100 V
Target ion current	200 mA ~ 1100 mA
Input power	150 W ~ 800 W
Pulse frequency	20 kHz ~ 100 kHz
Substrate	Glass slide
Film thickness	≒200 nm
Substrate temperature	50 ~ 110 ℃ (no heating)

3. RESULTS AND DISCUSSION

(a) Dependence on pulse width and input power

Figure 1 shows typical changes in deposition rate against the pulse width. Oxygen gas content in the sputtering gas was fixed at 3%. It is clear from the figure that the deposition rate increased as the pulse width increased and high rate deposition above 1 nm/sec was realized at a pulse voltage of 800 V.

Figure 2 shows X-ray diffraction diagrams of the film deposited at various pulse width. Pulse voltage was fixed at 500 V. The diffraction diagram changes little with pulse width and clear diffraction peaks are not observed in the diagram. This suggests that these films have amorphous structure. Average surface roughness Ra of these films evaluated from AFM measurement is shown in Fig. 3 against deposition rate. A clear dependence of Ra on the deposition rate was not observed and Ra took a value around 0.3 nm. This indicates that these films have very smooth surfaces.

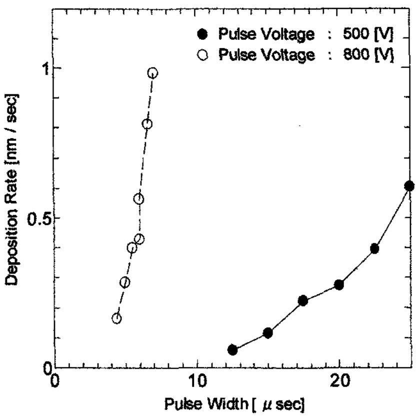

Fig. 1 Changes in deposition rate at different pulse widths at pulse voltages of 500 V and 800 V.

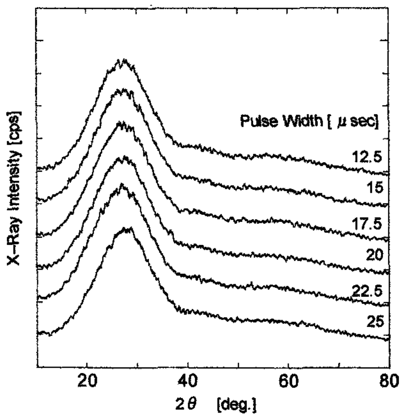

Fig. 2 X-ray diffraction diagrams of films deposited at various pulse widths. Pulse voltage was fixed at 500 V.

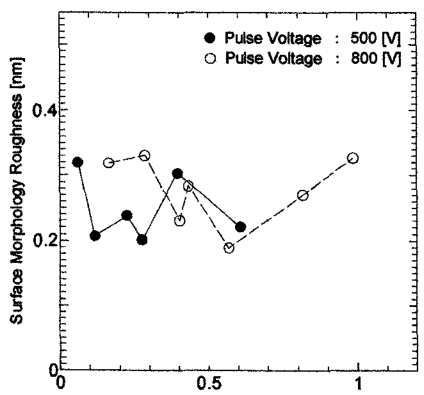

Fig. 3 Changes in surface roughness (Ra) of the films at various deposition rates, deposited at pulse voltages of 500 V and 800 V.

Figures 4, 5, and 6 show changes in the refractive index, transmittance and optical band gap of the film with deposition rate, respectively. The refractive index is the value at wavelength 500 nm. It decreases as deposition rate increases, while the optical band gap change in the other direction. The transmittance depends little on the deposition rate. The decrease in refractive index may suggest that the film has a porous structure with lower density, although the reason is not clear. The reason why optical band gap of the film increases with deposition rate as shown in Fig.6 is also not clear.

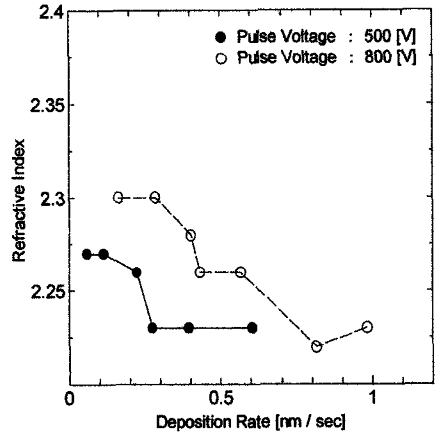

Fig. 4 Changes in refractive index of the film at various deposition rates, deposited at pulse voltages of 500 V and 800 V.

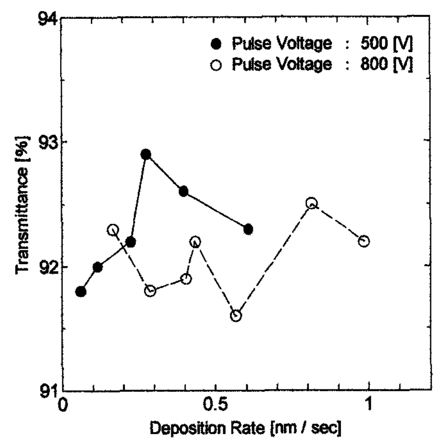

Fig. 5 Changes in transmittance of the film at different deposition rates, deposited at pulse voltages of 500 V and 800 V.

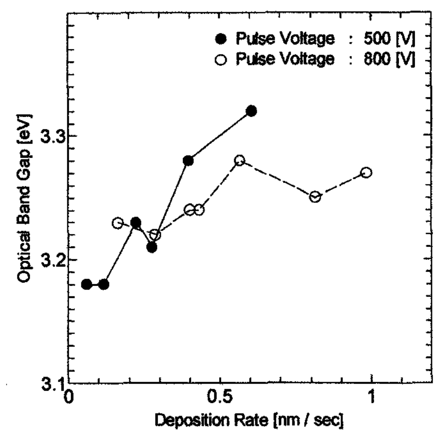

Fig. 6 Changes in optical band gap of the film at different deposition rates, deposited at pulse voltages of 500 V and 800 V.

(b) Dependence on oxygen gas content in sputtering gas

The deposition rate of TiO_2 film is known to strongly depend on the oxygen gas content in sputtering gas [7]. Similar result was observed in this study, as shown in Fig. 7. The deposition rate decreases sharply as the oxygen gas content increases. This decrease is thought to be due to changes in the target surface from an oxygen poor layer with high sputtering yield to a stoichiometric oxide layer with low sputtering yield.

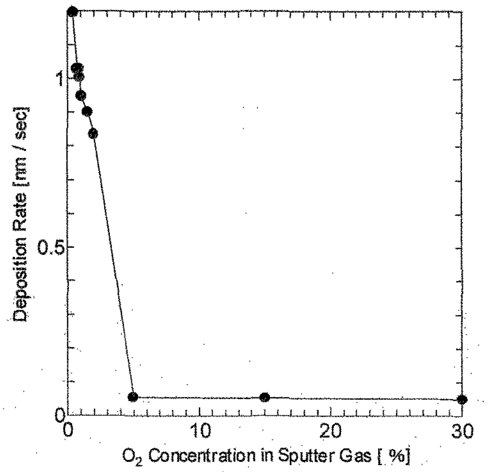

Fig. 7 Changes in deposition rate at different O_2 gas content in sputter gas.

Figure 8 shows changes in the X-ray diffraction diagrams of the film deposited at various pulse voltages. In the film preparation, oxygen gas content in the sputtering gas and input sputtering power was fixed at 30% and 500 W, respectively. Compared with the X-ray diffraction diagrams of the film deposited at a oxygen gas content of 3 % shown in Fig. 2, these films have clear diffraction peaks which correspond to rutile structure, although the diagram changes little with pulse voltages. These results suggest that crystallization in the film is promoted by the increase in the oxygen gas content of the sputtering gas.

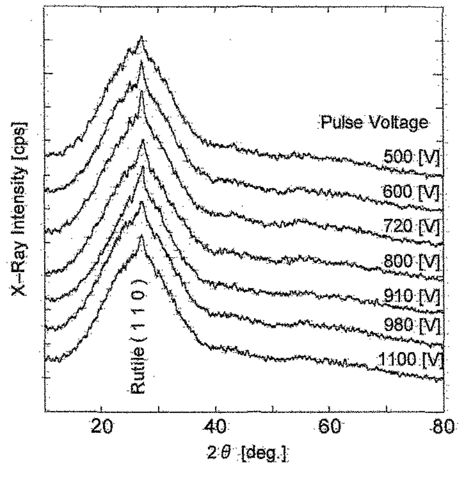

Fig. 8 Changes in X-ray diffraction diagrams of the film deposited at various pulse voltages. Oxygen gas content was fixed at 30 %.

Figure 9 shows typical AFM surface images of these films deposited at various oxygen gas content of sputtering gas. It is clear from the figure that the surface roughness significantly increases as the oxygen gas content increases. This seems to be attributable to the promotion of the crystallization in the films by the increase in oxygen gas content. Figure 10 shows changes in average surface roughness of these films against pulse voltage. Surface roughness depends mainly on the oxygen gas content, and also slightly on the pulse voltage.

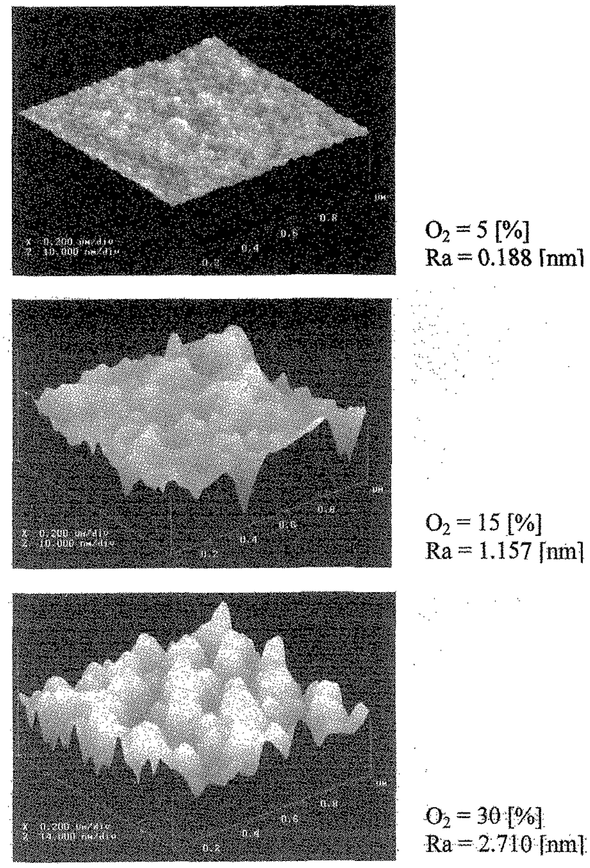

Fig. 9 Surface AFM images of the film deposited at various oxygen gas concentrations. Pulse voltage was fixed at 800 V.

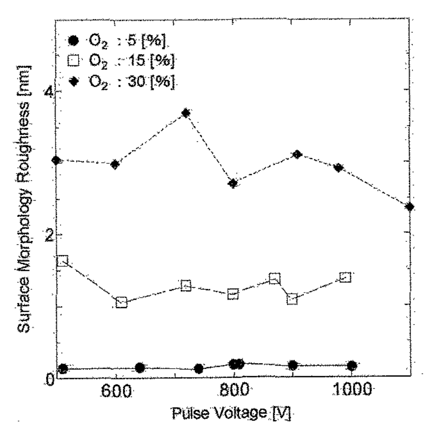

Fig. 10 Average surface roughness (Ra) of the film versus sputtering pulse voltage deposited at oxygen gas content of 5 %, 15 %, and 30 %.

Figure 11 is a plot of the refractive index of these films versus pulse voltage. The figure clearly shows that film deposited at a higher oxygen gas content has a larger refractive index which changes little with sputtering pulse voltage. The films deposited at 30 % oxygen gas content have a refractive index as large as 2.5. This may be due to the growth of crystallite with rutile structure in the films. These results indicate that sufficient oxygen supply to the film surface during deposition is necessary to obtain film with a large refractive index. In the sputtering at such a large oxygen gas content level, sputter emission of Ti atoms from the target surface is suppressed remarkably and most of the sputtered particles are composed of molecules such as TiO[8].

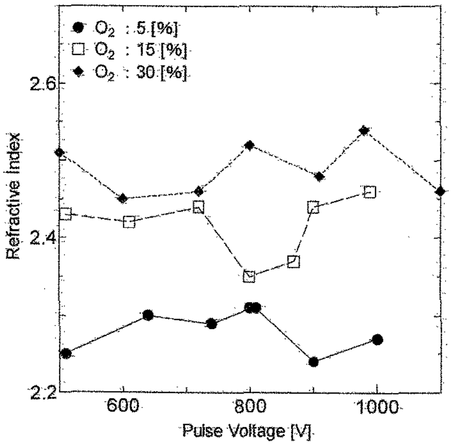

Fig. 11 Refractive index of the film versus sputtering pulse voltages deposited at oxygen gas content of 5 %, 15 %, and 30%.

The optical band gap of these films is shown in Fig.12, and the transmittance in Fig. 13 against sputtering pulse voltage. These figures indicate that both energy gap and transmittance decrease as the oxygen gas content increases, although the reason is not yet clear. The dependences of these optical properties on sputtering pulse voltage are not obvious.

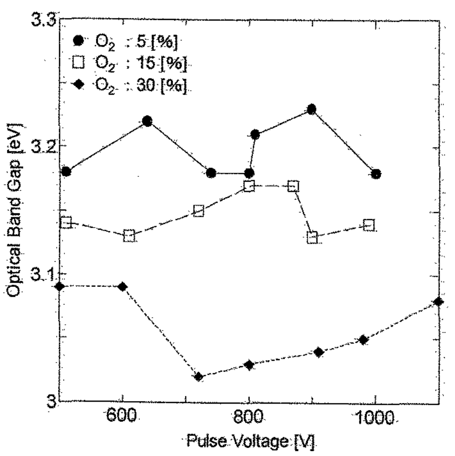

Fig. 12 Optical band gap of the film versus sputtering pulse voltages deposited at oxygen content of 5%, 15%, and 30%.

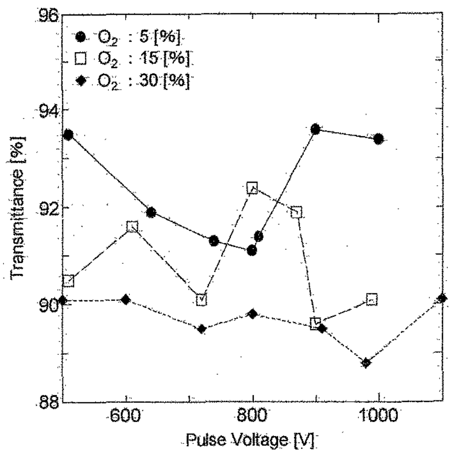

Fig. 13 Transmittance of the film versus sputtering pulse voltages deposited at oxygen gas content of 5%, 15%, and 30%.

4. Conclusions

High rate deposition of TiO_2 thin films was attempted using a pulse sputtering technique with oxide target. The following results were obtained.

(1) Deposition rate above 1 nm/sec was easily achieved by increasing input power. However, the deposition rate depended strongly on the oxygen gas content of the sputtering gas.

(2) The increase in the deposition rate led to a decrease in the refractive index and an increase in transparency. This suggests that the films deposited at a high deposition rate may have a porous structure with a low density. On the other hand, an increase in oxygen gas content in the sputtering gas led to an increase in the refractive index of the film as large as 2.5, and promoted crystallization in the film.

These results indicate that enough oxygen radicals should be supplied to the film surface during deposition to achieve high rate deposition of TiO_2 film with a large refractive index. However, the oxygen supply to the target surface needs to be suppressed to increase the sputtering rate.

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