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Dependence of Structure on the Oxygen Gas Flow Rate in Reactive Gas-Flow-Sputtering of TiO_2 Films

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Titanium dioxide films were deposited in an Ar-O_2 atmosphere at high pressure of 130 Pa by reactive gas flow sputtering (GFS). A pure Ti tube was used as the target and the O_2 gas was supplied in front of the substrate, resulting in a very stable discharge and a high deposition rate of about 100 nm/min. The crystal structure of TiO_2 films was found to strongly depend on the flow rate of O_2 gas during sputtering. The crystallinity of films became better with increase in the O_2 flow rate, but it suddenly became poor if the O_2 flow rate exceeded a value. There existed an optimum oxygen fraction for the formation of crystalline TiO_2 films. A highly (110)-oriented films of anatase phase with good crystallinity could be obtained at substrate temperature of 300 ℃, O_2 flow rate of 1 sccm and Ar flow rate of 300 sccm

Key words: titanium dioxide, titanium dioxide film, photocatalyst, sputtering, sputtered film, gas flow sputtering

1. INTRODUCTION

Titanium dioxide (TiO_2) films are widely used as optical coatings because of their excellent reliability and durability, and optical transmittance with high refractive index. In addition, TiO_2 thin films are now finding a widespread application for photocatalytic coatings [1, 2]. For the preparation of optical coatings, sputtering is a very useful method because it can fabricate high quality TiO_2 films; high density, strong adhesion, high hardness, etc., can be achieved at low substrate temperature. On the other hand, it has not been accepted that conventional sputtering methods can produce highly activated photocatalytic TiO_2 films, although there have been many researches concerning about photocatalytic activities of sputtered TiO_2 films [3-5].

Recently, Yamagishi et al. reported that TiO_2 films with high photocatalytic activities and photo-induced hydrophilicity were successfully deposited by reactive magnetron sputtering at the rather high pressure of 3 Pa [6]. Ishii et al. also showed that the gas flow sputtering (GFS) operating at a very high pressure of 130 Pa could deposit TiO_2 films with a high level of photocatalytic activity comparable to that of TiO_2 powder of anatase phase [7]. The reason for the improvement of photocatalytic activities by increasing Ar pressure is assumed as follows. Many kinds of energetic particles impinge on the substrate in a sputtering process. Ar reflected from the target and negative oxygen ions, O^-, accelerated by the cathode sheath have very high energies, sometimes over 100 eV [8, 9], and they often strike the substrate. The bombardment of these high-energy particles must create many structural defects in the film. It is thought that some structural defects in TiO_2 introduce defect levels in the mid-gap which could be recombination centers for photo-induced holes and electrons, resulting in poor photocatalytic activities [5]. If the Ar pressure is so high, the bombardment of energetic particles can be suppressed because of the thermalization of energetic particles [10], and high quality films showing superior photocatalytic activities will be obtained.

GFS [11, 12] is a high-pressure sputtering at about

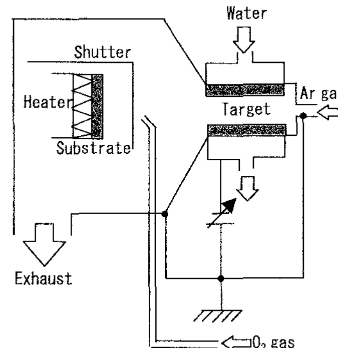

Fig. 1 Schematic diagram of reactive gas flow sputtering apparatus used for the preparation of TiO_2 films.

100 Pa; under such high-pressure conditions, the thermalization of energetic particles is completed [10] and "soft" film growth similar to that of chemical vapor deposition (CVD) occurs. In GFS, it has been observed that the crystal structure and the level of photocatalytic activity of TiO_2 films strongly depend on the flow rate of O_2 gas during sputtering [7]. In order to obtain highly activated photocatalytic TiO_2 films, the relationship between the structure and the O_2 flow rate is necessary to be known.

Thus, in this study, the crystal structure and morphology of TiO_2 films deposited under various conditions by reactive GFS were investigated, and the phase diagram as the function of substrate temperature and O_2 fraction was obtained.

2. EXPERIMENTAL

Figure 1 shows a schematic diagram of the GFS apparatus used for the preparation of TiO_2 films. The target was a 99.9% Ti tube with the internal diameter of 7 mm and length of 50 mm. Ar gas of 99.9999% purity was used as the sputtering gas, and it was introduced to flow through the target. On the other hand, O_2 gas was

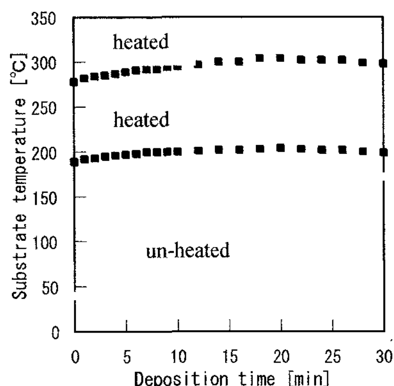

Fig. 2 Substrate temperatures as a function of deposition time when the substrate was heated at two levels and unheated.

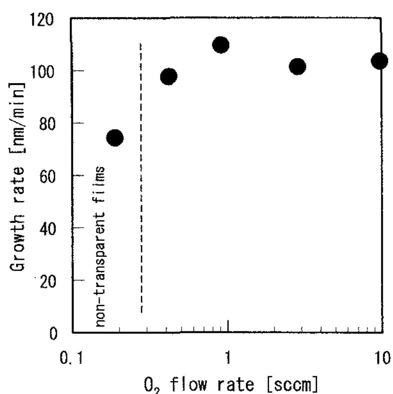

Fig. 3 Growth rates of the films deposited at various O_2 flow rates.

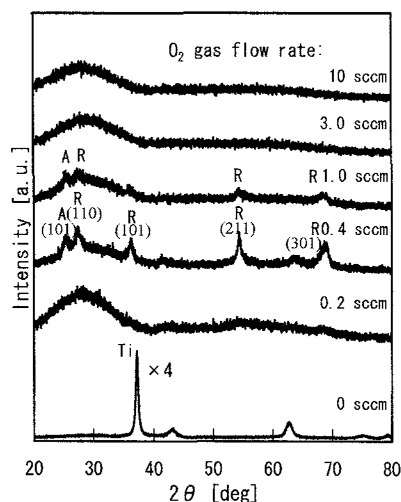

Fig. 4 XRD patterns of TiO_2 films deposited at various O_2 flow rates; the substrate was unheated. R and A indicate the reflections from rutile and anatase phases, respectively.

added to the stream of Ti vapor near the outlet of the target. The chamber was evacuated to 4×10^{-4} Pa prior to

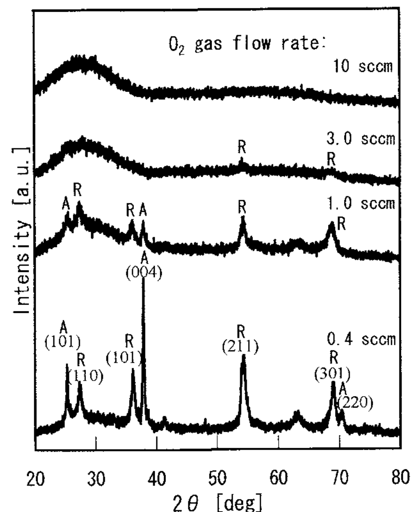

Fig. 5 XRD patterns of TiO_2 films deposited at various O_2 flow rates; the substrate was heated at 200 ℃. R and A indicate the reflections from rutile and anatase phases, respectively.

the sputtering. The total pressure during sputtering was maintained at 130 Pa under the condition of a flow rate of 300 sccm for Ar gas and a flow rate from 0 to 10 sccm for O_2 gas. Specimen films were obtained at target-to-substrate separation of 5 cm and discharge current of 1.0 A. Fused silica plates were used as the substrate, which was placed on the heater, and its temperature was monitored using an AC thermocouple. The substrate was heated at 200 ℃ and at 300 ℃. Figure 2 shows the changes in substrate temperature Ts as a function of deposition time for the two cases. It can be seen from the figure that the substrate temperature was well controlled at 200 ℃ and 300 ℃. On the other hand, when the substrate was not heated, its temperature rose gradually to about 150 ℃ in 10 min and became about 160 ℃, as shown in Fig. 2. Although the main factors responsible for heating of the substrate in this heated in the target are thought to play important roles.

Film thickness was estimated from the step difference of the masked part after peeling off the mask; the step difference was measured by a profilemeter. The crystal structure was characterized by conventional x-ray diffraction (XRD) (Cu Kα radiation was used), and the morphology was determined by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

Transparent films were obtained when O_2 gas was added at a flow rate higher than 0.3 sccm. On the other hand, the discharge was very stable and the discharge characteristics were unchanged if O_2 gas was supplied at flow rates ranging from 0 to 10 sccm. This indicates that O_2 gas can not penetrate the target due to Ar gas counter flow and the target inner-surface is not oxidized during the sputtering. Figure 3 shows the film growth rates obtained at various values of Fo. It can be seen from this figure that the growth rate does not so change if Fo increases in the growth region of transparent films. It is

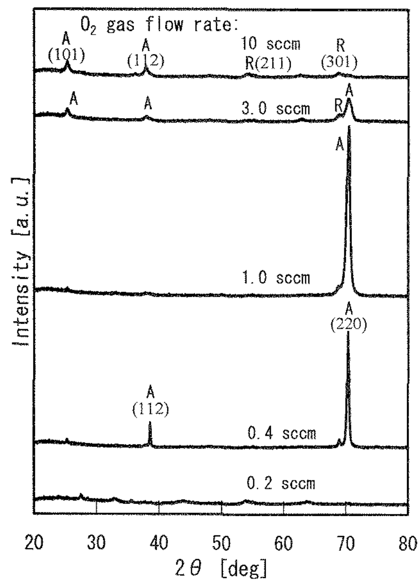

Fig. 6 XRD patterns of TiO_2 films deposited at various O_2 flow rates; the substrate was heated at 300 ℃. R and A indicate the reflections from rutile and anatase phases, respectively.

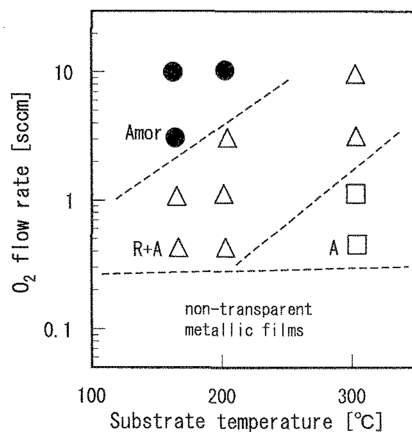

Fig. 7 Schematic phase diagram indicating the formation ranges of anatase (A), amorphous (Amor) and the mixture of rutile and anatase (R+A) as the function of substrate temperature and O_2 gas flow rate.

noteworthy that the growth rate of TiO_2 films obtained in GFS, i.e., about 100 nm/min, is much higher than that of magnetron sputtering [4, 5].

The crystal structure of the films deposited for 30 min under various values of Ts and Fo was characterized by XRD. Figure 4, Fig. 5 and Fig. 6 show the XRD patterns of the films deposited on the substrates unheated, heated at 200 ℃ and at 300 ℃, respectively. The thickness of specimens was about 3 μm. Titanium dioxide occurs in three crystalline phases: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). In the films obtained in this study, brookite phase was not clearly observed in every film, and rutile and anatase or their mixture was observed. A

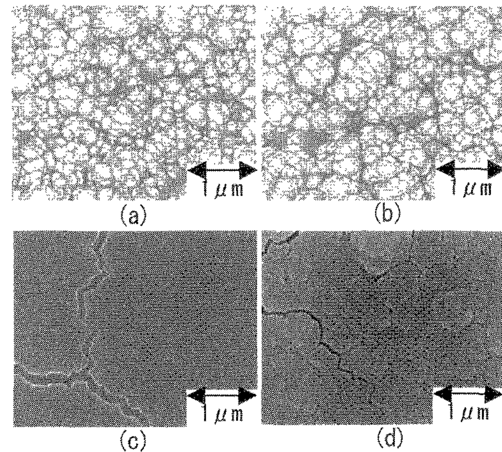

Fig. 8 SEM images of TiO_2 films deposited at various O_2 flow rates on the unheated substrates; the O_2 gas flow rate was (a) 0.4 sccm, (b) 1.0 sccm, (c) 3.0 sccm and (d) 10 sccm.

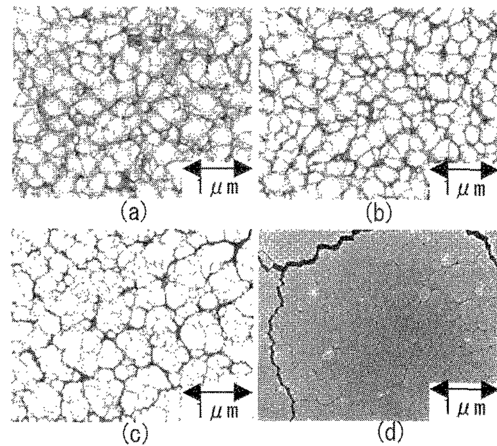

Fig. 9 SEM images of TiO_2 films deposited at various O_2 flow rates on the substrates heated at 200 ℃; the O_2 gas flow rate was (a) 0.4 sccm, (b) 1.0 sccm, (c) 3.0 sccm and (d) 10 sccm.

similar Fo dependence of crystal structure was observed for both films deposited on the unheated substrates and deposited on the substrates heated at 200 ℃; that is, TiO_2 films consisting of rutile and anatase phases grew at low Fo, while amorphous films grew at large Fo. This tendency can be seen in Fig. 4 and Fig. 5. On the other hand, when Ts=300 ℃, anatase films were obtained at low Fo and rutile phase becomes to be mixed in anatase phase with increasing Fo over 3 sccm, as shown in Fig. 6. An evolution of the diffraction peak from (220) plane of anatase phase for the film obtained at Fo=1 sccm indicates the development of strong texture with the crystallographic orientation of the (110) plane parallel to the film plane. In this case, amorphous films did not grow if Fo was increased up to 10 sccm. A noteworthy feature seen in Fig. 6 is that the intensity of diffraction peaks becomes strong, indicating the improvement of crystallinity, as Fo is increased, but it becomes weak if Fo exceeds 3 sccm.

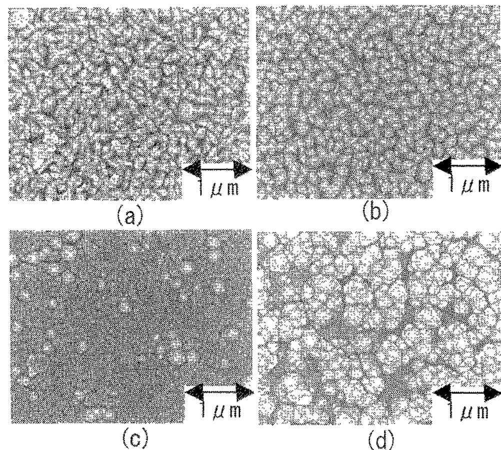

Fig. 10 SEM images of TiO_2 films deposited at various O_2 flow rates on the substrate heated at 300 ℃; the O_2 gas flow rate was (a) 0.4 sccm, (b) 1.0 sccm, (c) 3.0 sccm and (d) 10 sccm.

Figure 7 shows the phase diagram of TiO_2 films as the function of Fo and Ts, which summarize the results of XRD. There have been reported many experimental results about the crystal structure of sputtered TiO_2 films [3-6, 13]; but it has never been observed that the phase formation is strongly dominated by oxygen partial pressure, and especially that an atmosphere of high oxygen fraction prevents the crystallization. Zeman et al. investigated the crystal structure as the function of total pressure and oxygen partial pressure for reactive rf magnetron sputtering of TiO_2 films, and found that the total pressure had a stronger effect on the phase composition and the crystallinity compared to the oxygen partial pressure, and also found that the increase in oxygen partial pressure rather resulted in the improvement of film crystallinity [4]. This distinguished difference will be resulted from the difference in an operating pressure; GFS operates at about 100 Pa, while rf magnetron sputtering is performed at the pressure lower than 3 Pa. Since a film growth like that of CVD occurs in GFS, a chemical reaction between Ti atoms and oxygen is assumed to play an important role.

It was found that the film morphology also depended on Fo. Figure 8, Fig. 9 and Fig. 10 show the surface SEM images of the films deposited on the substrate unheated, heated at 200 ℃ and at 300 ℃, respectively; the samples shown in these figures were the films shown in Fig. 4, 5 and 6, respectively. It is generally observed for sputtered films that polycrystalline films have a grain structure with distinct grain boundaries while amorphous-like films have very flat surface. By comparing the phase diagram obtained by XRD and these SEM images, it is clearly found that this tendency can be applied to the TiO_2 films obtained in this study. On the other hand, many clucks are seen in amorphous films. They are assumed to be formed due to a large difference in thermal expansion coefficient β between TiO_2 ($\beta \simeq 8\times10^{-6}$ K^{-1}) and SiO_2 substrate ($\beta \simeq 0.5\times10^{-6}$ K^{-1}). Similar clucks are unseen in crystallized films. The reason is assumed to be that the residual stress is relieved by a large number of grain boundaries.

4. CONCLUSIONS

The structures of TiO_2 films obtained in an atmosphere of 130 Pa by reactive GFS were investigated, and the phase diagram as the function of substrate temperature and oxygen partial fraction was obtained. It was found that the crystallinity was improved by increasing the substrate temperature, but found that a high fraction of oxygen gas resulted in a poor crystallinity and an optimum oxygen fraction for the crystal growth existed. A highly (110)-oriented films of anatase phase with good crystallinity could be obtained at 300 ℃ by adjusting O_2 flow rate at 1 sccm.

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