The relationships between the film structure and photocatalytic characteristics of TiO₂ films deposited under oblique incidence by oxygen ion assisted reactive evaporation (OIARE) method.

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We deposited the TiO₂ films at various oxygen ion accelerating voltages under oblique incidence by using OIARE method and investigated the relationships between their structures and photocatalytic performances. The films deposited at 350 °C, the accelerating voltage of 200 eV, and substrate tilt angle of 35 degree had excellent photocatalytic performance of 17.7 [μmol·l⁻¹·min⁻¹] for the decomposition of methylene-blue. The film has anatase structure with mean surface roughness Ra of 11.4 nm and mean crystallite size of 18.0 nm. The photocatalytic performance takes a maximum value around 200 eV and decreases monotonically with further increase of the accelerating voltage. The mean crystallite size of the film was decreased from 20.8 nm to 14.3 nm by the increase of the oxygen ion accelerating voltage from 0 to 1000 eV, which suggests that the high energy oxygen ion bombardment to the film surface will produce damages in the film and degrading the performance of the film. These results indicate that control of the energy of oxygen ions incident to the film surface is important to obtain a film with excellent photocatalytic properties.

Keyword: Titanium dioxide (TiO₂) film, Photocatalytic, Oxygen ion assisted reactive evaporation method

1. Introduction

Titanium dioxide (TiO₂) is well known as a photocatalyst because of the strong oxidizing power of photogenerated holes¹. When the TiO₂ is illuminated by UV light with higher energy than the TiO₂ band gap, an inter-band transition can be induced, resulting in the generation of electron-hole pairs. Such excited electrons or holes can diffuse to the TiO₂ surface and generate various radicals or ions which can decompose organic compounds adsorbed on the TiO₂ surface². Its photoinduced self-cleaning properties in particular have attracted considerable attention in various application fields. Photoinduced hydrophilicity has been observed on rutile or anatase TiO₂ surfaces, where the water contact angle decreased to less than 1.0 degree after UV illumination in air³.

So far, various methods were proposed for preparing TiO₂ films. They include sol-gel, dip coat, binder, spray, thermal spray, sputtering, chemical vapor deposition, ion plating, and oxygen ion assisted reactive evaporation (OIARE) methods^{4,5}. In the method, vacuum evaporation of titanium (Ti) and oxygen ion irradiation are combined to obtain a film with high density and excellent crystalline⁶⁻⁹. In our previous papers, we reported that the OIARE can not only realize very high deposition rate greater than 100 nm/min, but also deposit crystallized TiO₂ films at a low substrate temperature below 100 °C. It is noteworthy that the OIARE method enables precise control of the crystallographic structure of the films, since titanium atoms and oxygen ions with a desired energy can be supplied independently to the substrate from an evaporation source and an ion source, respectively.

In this research, we deposited the TiO₂ films at various oxygen ion accelerating voltages under oblique incidence by using OIARE method and were investigated the relationships between their structures and photocatalytic performances¹⁰⁻¹⁴.

2. Experimental Details

Figure 1 shows the deposition system used for this study. The OIARE apparatus, with a plasma source (IBD-5-1; Hitachi Ltd.), consists of a titanium electron beam evaporation source (Ti source), an ECR oxygen plasma source, and a sample holder. The Ti source was separated from the deposition chamber, as shown in Fig. 1, and Ti atoms were transported to the substrate through stainless steel meshes. The distance from the substrate to the source and the distance from the substrate to the ECR oxygen plasma source are 370 mm and 480 mm, respectively.

Fig. 1. OIARE system used in this study.

The deposition chamber was evacuated to a background pressure of less than 7.5×10^{-7} Torr using a rotary pump (RP) and turbo molecular pump (TMP). The oxygen gas pressure in the chamber was 8.6×10^{-4} Torr when an oxygen gas of 99.999% purity was introduced into the chamber at the gas flow rate of 50 sccm through the ECR plasma source. Input power for the ECR plasma source was fixed at 600 W.

The deposition rate was fixed at about 15.6 nm·min⁻¹ by adjusting the amount of injection electron current of the electron beam gun. The substrate temperature was fixed at 350 °C, and oxygen ion accelerating voltages were changed in the range from 0 to 1000 eV. Substrate tilt angle was fixed at 35° where the incidence angle of titanium atoms to the substrate was 55°.

Typical film preparation conditions are listed in Table I.

Table I. Typical film preparation conditions.

Deposition apparatus	OIARE
Back ground pressuer [Torr]	$<7.5 \times 10^{-6}$
Substrate for the sample	Non-alkali glass
Substrate heating temperature [°C]	350
Oxygen gas flow rate [sccm]	50.0
Electron beam gun emission [mA]	210-490
Electron beam gun voltage [kV]	9
Microwave power [W]	600
Oxygen ion accelerating voltage [eV]	0-1000
Deposition rate [nm/min]	15.6
Substrate tile angle [degree]	35.0
Film thickness [nm]	1000

Titanium solid metal blocks of 99.99 % purity were used as the evaporation material. Non-alkali sheet glass (No.1737; Matsunami Glass Ind. Co., Ltd.) of 60×60 mm size was used as the substrate.

The film thickness was measured using a surface profiler (Decktak 3030; Solan Technology Corp.). The crystal structure of the TiO₂ film was evaluated using X-ray diffractometry (XRD, RINT2000/PC; Rigaku Corp.). The surface morphology of the film was investigated using atomic force microscopy (AFM, NanoScope III; Digital Instrument Co., Ltd.) and field-emission scanning electron microscopy (FE-SEM, S-5000; Hitachi High-Technologies Corp.). Transmittance of the film was measured using a spectral photometer (V-550; Jasco Inc.).

The hydrophilicity performance was evaluated by measuring the changes in the contact angles of pure water using a contact angle measuring system (OCA 15plus; Data Physics Corp.). The organics-decomposition performance was measured from the change in the methylene-blue concentration. In the evaluations, black light of main wave length at 352.0 nm was used as the UV source and the measurement was carried out under the UV irradiation at 1.0 mW·cm⁻².

3. Results and Discussion

3.1 Structure of the films

Figure 2 shows XRD diagrams of TiO₂ films deposited at various oxygen ion accelerating voltages.

It is clear from the figure that only the peaks that are characteristic of anatase were observed such as (101) plane at around $2\theta = 25.2^\circ$, and poly-crystalline anatase film with random orientation was obtained. The (101) and (211) plane peak intensity was increased by the increase of the acceleration voltage of oxygen ions. This indicates that the increase in the ion energy promotes the crystallization of the TiO₂ films.

On the other hand, the crystallite size of these films estimated from the (101) and (211) plane diffraction peak using Scherrer's equation was decreased monotonically with the increase of the accelerating voltage as shown in Figure 3. This fact suggests that the increase in the accelerating voltage also causes the formation of defects

in the films. Therefore, the incidence of high energy oxygen ions has two effects; one is promotion of the crystallization in the film and the other is the creation of damages in the films through the ion bombardment for the film surface.

Fig. 2 XRD diagrams of the films deposited at various oxygen ion accelerating voltages.

Fig. 3 Mean crystallite size [D] of the films deposited at various oxygen ion accelerating voltages.

Surface morphologies of these films investigated by using AFM are shown in Figure 4.

Mean surface roughness Ra of the films was increased from approximately 10 to 18 nm as the oxygen ion accelerating voltages increased from 0 to 1000 eV.

Fig. 4 Surface AFM images of the films deposited at various oxygen ion accelerating voltages.

Figure 5 shows surface FE-SEM images of these films. It is evident from the figure that 5-10 sub-grains groups together and forms large grains with a diameter approximately from 100 to 300 nm. The size of the large grain increases as the oxygen ion accelerating voltage

increases and the film deposited at the accelerating voltage of 1000 eV has very large grains above 300 nm. This result may be caused by the promotion of crystallization by the increase of oxygen ion energy.

Fig. 5 Surface FE-SEM images of the films deposited at various oxygen ion accelerating voltages.

Figure 6 shows cross-sectional FE-SEM images of the films deposited at various oxygen ion accelerating voltages.

Every film has inclined columnar structure which was originated in the oblique incidence of titanium atoms to the substrate surface. Clear differences between the films were not observed, although surface roughness seems to increase with the increase of accelerating voltage.

Fig. 6 Cross-sectional FE-SEM images of the films deposited at various oxygen ion accelerating voltages.

3.2 Transmittance Spectra of the Films

Figure 7 shows transmittance spectra of films deposited at various oxygen ion accelerating voltages.

It should be noted that the transmittance in visible region of the film decreases remarkably as the oxygen ion accelerating voltage increases. This decrease in the transmittance is thought to be mainly caused by the light scattering in the films, since the film composed of large grains shown in Fig.5 becomes clouded and looks milky color, which is usually observed in the film deposited at a large accelerating voltage.

Fig. 7 Transmittance spectra of the films deposited at various oxygen ion accelerating voltages.

3.3 Photocatalytic Characteristics

3.3.1 Hydrophilicity performance

Figure 8 shows changes in the contact angles of water droplets on the film surface with the irradiation time of black light.

The contact angles of these films before UV irradiation have values between from 4.0 to 20.0 deg. The contact angle decrease steeply by the irradiation of the black light, and all the films obtained in this study show the super hydrophilicity after the UV irradiation for 20 min. However, it should be noted that the increase in the ion accelerating voltages above 800 eV leads to poor hydrophilicity of the film.

Fig. 8 Changes in the contact angles of water with UV irradiation for the films deposited of various oxygen ion accelerating voltages.

3.3.2 Organics-decomposition performance

Figure 9 shows changes in the concentrations of methylene-blue (MB) with UV irradiation time to the films. From the changes of the MB concentration by the UV irradiation, we calculated the decomposition performance index¹⁵ of the film (calculate a slope by using the least-squares method from the four selected points that show the largest change in the linear region of the MB concentration vs. UV irradiation time.).

The performance index of these films takes a value in the range from 3.7 to 17.7 [$\mu\text{mol}\cdot\text{l}^{-1}\cdot\text{min}^{-1}$]. It should be noted that the film with highest performance index of 17.7 [$\mu\text{mol}\cdot\text{l}^{-1}\cdot\text{min}^{-1}$] was obtained at the oxygen ion accelerating voltage of 200 eV.

Fig. 9 Changes in MB concentration with UV irradiation for films deposited of various oxygen ion accelerating voltages.

Figure 10 shows relationships between the average surface roughness Ra and decomposition performance index at various oxygen ion accelerating voltages.

It is evident from the figure that the decomposition performance index takes a maximum value of 17.7 [$\mu\text{mol}\cdot\text{l}^{-1}\cdot\text{min}^{-1}$] at a accelerating voltage around 200 eV. Further increase in the accelerating voltage degrades the decomposition performance of the film. This suggests that the increase in the accelerating voltage above 200 eV causes the formation of defects in the film, since the organics-decomposition performance was decreased by the production of damages (oxygen defect etc.) in the film¹⁶⁻¹⁸. Because the damages (oxygen defect etc.) in the crystallites work as the recombination center for electrons and holes. Therefore, the damage control is necessary to improve the photocatalytic characteristics of the films.

The surface roughness of the film increases gradually as the accelerating voltage increases, and the relationship between the surface roughness and organic decomposition performance seems to be little as shown in Fig.10.

Fig. 10 relationships between the surface roughness average Ra and decomposition performance index with oxygen ion accelerating voltages.

4. Conclusion

We deposited the TiO₂ films at various oxygen ion accelerating voltages under oblique incidence by using OIARE method, and investigated their structure and photocatalytic performances.

It became clear that the increase in the energy of incident oxygen ions not only promotes crystallization and grain growth in the TiO₂ films, but also induces damages in the TiO₂ crystallites. As a result, organic decomposition performance index takes a maximum value at a proper accelerating voltage. The highest organic decomposition performance index obtained in this work was 17.7 [$\mu\text{mol}\cdot\text{l}^{-1}\cdot\text{min}^{-1}$] at an accelerating voltage around 200 eV.

These results indicate that control of the energy of oxygen ions incident to the film surface is important to obtain a film with excellent photocatalytic properties.

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