Fabrication of Photocatalytic TiO₂ Films on Pure Aluminum Plates

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TiO₂ films were formed on aluminum plates by a dip-coating in an advanced sol-gel precursor solution, and the effect of sintering conditions on the photocatalytic properties of the oxide were investigated by UV adsorption. The samples prepared in this way exhibit photocatalytic activity in a range of suitable sintering conditions compatible with the region of crystallization of anatase characterized by X-ray diffraction. The surface morphology and adhesion between the TiO₂ nano-film and aluminum plate were confirmed by energy filtering transmission electron microscopy, and the surface morphology was found to affect the photocatalytic activity. The TiO₂ film was 30 nm thick and was confirmed to be finely crystalline with a mean diameter of 12 nm.

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1. Introduction

Recently, titanium dioxide (TiO₂) is focused on a photocatalytic material with potential application in reducing the environmental load of various manufacturing process.¹⁻³⁾ Although there are a few reports of the fabrication of TiO₂ thin films by wet method using TiO₂ precursor solution,³⁾ there are many reports of the application of anatase particles with binder materials by painting,⁴⁾ and by chemical vapor deposition²⁾ on the surface of the metal plates. Recently, Leprince-Wang and Yu-Zhang successfully fabricated TiO₂ thin-films of 20 to 73 nm thickness on Si wafer by electron beam evaporation,⁵⁾ and concluded that surface roughness increases with thickness of the TiO₂ film due to the development of a columnar structure of the TiO₂. However, they were unable to clarify the effect of TiO₂ thickness on its photocatalytic activity. Rengakuji *et al.* developed a new TiO₂ precursor-solution³⁾ produced by the repeated hydrolysis and polymerization of titanium alcoxide. The precursor solution was developed specifically to have an extended sol lifetime, but otherwise is similar to conventional sol-gel system. Rengakuji *et al.* refer to this as the advanced sol-gel method,⁶⁾ and have fabricated TiO₂ films on various ceramics substrates by dip-coating in such precursor solution,⁷⁾ with good results in terms of the photocatalytic properties of TiO₂.⁸⁾ The photocatalytic activity was found to vary according to the type of ceramic substrates.

In the present study, a precursor TiO₂ solution prepared by the advanced sol-gel method is used to fabricate TiO₂ film on pure aluminum plates by dip-coating. It is expected that a fabrication of TiO₂ films on aluminum plates can be realized maintenance-free curtain walls of buildings.⁹⁾ Their photocatalytic activity of the films is examined and related to sintering condition, and suitable fabrication conditions are proposed. The surface morphology and adhesion between the TiO₂ nano-film and the aluminum plate are characterized by

energy filtering transmission electron microscope (EFTEM) using cross-sectional samples for TEM (X-TEM). EFTEM has recently been employed for the analyses of semiconductor materials, and has been demonstrated to provide useful information regarding the distribution of elements in samples on the nanometer-scale.¹⁰⁻¹²⁾

2. Experimental

2.1 Fabrication of TiO₂ films

Aluminum ingot of 99.99% purity was cut to 10 mm thickness, hot- and cold-rolled down to 1.5 mm, cut out to plates of 40 mm × 30 mm. These aluminum plates were annealed at 573 K for 3.6 ks. The TiO₂ precursor solution was prepared by the advanced sol-gel method.³⁾ A cluster model of TiO₂ precursor solution is shown in Fig. 1.³⁾ Aluminum plates were then dip-coated in the TiO₂ precursor solution. The plate was lifted up, held and then raised at a constant speed of 0.165 to 0.408 mm/s. The coated plates were then sintered for between 1.8 ks and 21.6 ks, and cooled to room temperature in the furnace.

2.2 Evaluation of photocatalytic property

The photocatalytic activity of the sintered specimens was measured using a photocatalysis analyzer (PCC-1, Sinku-Riko, Japan). In this analysis process, the specimens were painted methylene blue and irradiated with ultraviolet (UV) light. The temporal change in the UV absorption of the films (ΔABS)¹³⁾ corresponds to the capacity of dissolution of methylene blue via photocatalysis. The UV light was used the UV black light of 1 mW/cm², and ΔABS was measured in air. A thin-film X-ray diffractometer (XRD-6000, Shimadzu, Japan) was used to identify the crystal structure of the TiO₂ films, and the surface features of the specimen were observed by a scanning electron microscope (SEM; S-3500H, Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) was employed to confirm the chemical composition

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Fig. 1 Schematic illustration of titanate oligomer (titanium oxide cluster).

of the oxide layer using Mg-K α X-ray source (1253.6 eV, PHI Model 04-151, Perkin-Elmer, USA) at 10 kV and 40 mA. A double-pass cylindrical mirror analyzer (PHI Model 15-255G, Perkin-Elmer, USA) was operated at a sweep rate: of 0.02–1.0 eV/s and pass energy of 50–100 eV.

2.3 Preparation and observation of X-TEM samples

X-TEM samples were prepared by focused ion beam (FIB) milling and mechanical extraction, which is referred to as “the picking-up technique”,¹⁴⁾ as follows. Platinum was deposited on the TiO₂-coated Al plate by an ion-coater to create an electrically conductive layer in preparation for FIB milling. A strip of carbon was then deposited on the surface to protect the TiO₂ nano-film in the FIB chamber, and the section was milled out by milling 10 μm $\times$ 3 μm $\times$ 10 μm holes on either side of the section, creating a narrow (200 nm) wall between the holes. The sample was then tilted by about 60° in order to mill the bottom of the wall, and one side connecting the wall to the TiO₂-coated Al plate was also milled. A small tip of the cross-section of the TiO₂-coated Al sample was produced in this way, and was picked up using a glass probe, picked up and mounted on a carbon film supported by copper grid. The thickness of this tip was estimated to be less than 200 nm according to its convergent beam electron diffraction (CBED) pattern obtained by TEM (EM-002B, Topcon, Japan) at 200 kV. These samples are somewhat thick for high-resolution TEM observation but sufficient to construct bright field images and elemental maps by EFTEM. The EFTEM (4010T, JEOL, Japan) was used with GIF-200 energy-filter (Gatan Inc., USA) and operated at 400 kV. Elemental maps were taken using three windows under the conditions listed in Table 1.

3. Results and Discussion

3.1 Effect of sintering temperature

Figure 2 shows the change in ΔABS with UV irradiation time for samples sintered at temperature between 523 and 773 K, indicating the photocatalytic activity of the samples. At the lowest sintering temperature of 523 K (Fig. 2(a)), ΔABS remains virtually unchanged, only decreasing slightly after extended irradiation time. Here, we can define negligible photocatalytic activity as ΔABS smaller than -0.005 , low activity as smaller than -0.01 , and acceptable photocatalytic activity as larger than -0.01 . Hence, this sample exhibits

Table 1 Details of the acquisition of elemental maps for X-TEM sample.

	Ti	O	Al
Pre-edge 1 (eV)	416	497	1470
Pre-edge 2 (eV)	436	517	1520
Post edge (eV)	456	532	1560
Slit width (eV)	10	10	30
Acquisition time (s)	30	30	60

little photocatalytic activity. The sample sintered at 573 K shown in Fig. 2(b) exhibited a greater response, yet was still relatively constant. The ΔABS of samples prepared at 623 and 673 K in Figs. 2(c) and (d) decreased remarkably with irradiation time, and exhibit the optimal photocatalytic activity with respect to sintering time and irradiation time. At higher temperatures in Figs. 2(e) and (f), the photocatalytic activity again decreased to quite low values. The sample sintered at 673 K for 3.6 ks is the most appropriate specimen with respect to both the shortest sintering time and the optimal photocatalytic activity.

3.2 Effect of lifting-up speed

In general, the photocatalytic activity of TiO₂ is controlled by its crystal structure, and high photocatalytic activity is obtained at a critical temperature that yields an anatase structure.¹⁵⁾ X-ray diffraction measurements were performed in order to detect the peaks of anatase structure, and low peaks of anatase structure of 25.3° ($\{101\}$) and 38.6° ($\{112\}$) were obtained from the samples sintered at 673 K as shown in Fig. 3(a). A peak of 25.3° was just used to identify for anatase structure, because a peak of 38.6° for an anatase structure is more weaker than 25.3°, which could not be confirmed actually, and a peak of 38.4° for aluminum ($\{111\}_{\text{Al}}$) superimposes with a peak of 38.6° for an anatase structure. This suggests that the TiO₂ film was probably too thin. The lifting-up speed V was then controlled so as to vary the thickness of the TiO₂ films. The results for the samples sintered at 673 K for 3.6 ks are shown in Fig. 4. The photocatalytic activity of the sample lifted up at 0.248 mm/s was higher than that lifted up at the original V of 0.165 mm/s, however, higher lifting-up speeds produce films with the same photocatalytic activity as that of the original film. The film thickness appears to increase with lifting-up speed up to a critical speed V_c as a result of the solidification of the precursor solution before

Fig. 2 Changes in ΔABS with UV irradiation time (t_{UV}) of samples sintered at (a) 523 K, (b) 573 K, (c) 623 K, (d) 673 K, (e) 723 K and (f) 773 K.

running back into the bath. Here, V_c appears to be around 0.248 mm/s, above which the morphology of film surface produced is thought to become wavy and non-uniform, resulting in a reduction in photocatalytic activity. The peak assigned to the anatase structure of 25.3° becomes intense with increasing V , particularly for the sample lifted up at 0.408 mm/s. It seems that the absence of anatase peak is attributable to the weak response of the thin layer.

3.3 Suitable conditions to form TiO₂ films

We have therefore clarified that there is a critical lifting-up speed, and a clear relationship between sintering temperature and sintering time for the fabrication of TiO₂ films on aluminum plates with respect to photocatalytic activity. Figure 5 shows a summary of the suitable fabrication conditions for this system. Open and closed circles, and open triangles show that optimal, acceptable and poor photocatalytic activities of TiO₂ films. There is a region of sintering conditions that are suitable for forming TiO₂ films with high photocatalytic activity on aluminum plate. The anatase crystallization conditions are also shown. The surface morphologies of TiO₂ films, as

Fig. 3 X-ray diffraction patterns for TiO₂ films on Al plates sintered at 673 K for 3.6 ks and lifting-up speed (V) of (a) 0.165, (b) 0.248, (c) 0.323 and (d) 0.408 mm/s.

obtained SEM, are shown in Fig. 6 for samples sintered at 623, 673 and 723 K for 3.6 ks. The samples sintered at 623

Fig. 4 Changes in ΔABS of samples formed at several lifting-up speeds (V) prior to sintering at 673 K for 3.6 ks.

Fig. 5 Relationship between sintering temperature and sintering time with respect to photocatalytic activity.

and 723 K exhibit scratches and peeling, whereas the sample sintered at 673 K had a smooth surface. This is not an essential reduction of photocatalytic activity of samples, but, it is important for industrial applications of this advanced sol-gel method and ΔABS method, which is significantly affected the surface condition of samples on the response for the change in ΔABS .

3.4 Observation of X-TEM sample

The morphology and TEM image of the X-TEM is shown in Figs. 7(a) and (b). The central dark line in Fig. 7(b) was the TiO_2 film, the lower layer was the aluminum plate, and the upper layer was the protective carbon. The Pt layer was located between the carbon and TiO_2 . Figure 8(a) shows a zero-loss image of the area marked in Fig. 7(b). The interface between the Pt-layer and the TiO_2 film was very flat. No cracks were observed between TiO_2 nano-film and aluminum plate, although a layer of unknown composition did exist between them. Figures 8(b) to (d) are elemental maps of the X-TEM sample obtained by EFTEM to confirm the chemical composition of each layer. The TiO_2 film was almost 30 nm thick, and can be seen more clearly than in the zero loss image. This thickness of 30 nm is consistent with that measured by atomic force microscopy in a previous study.⁸⁾ As region of Ti was clear in Fig. 8(b) and does not extend into the underlying Al, indicating that Ti did not diffuse into the aluminum plate when the sample is sintered. As the TiO_2 film overlaps with the unknown-layer in the O-map, the unknown-layer is

Fig. 6 SEM images of surface morphologies of samples sintered for 3.6 ks at (a) 623, (b) 673 and (c) 773 K.

expected to be Al_xO_y . The Al of the aluminum plate also overlaps this Al_xO_y region in the Al-map. Figure 9 shows an HRTEM image of the TiO_2 film. Lattice fringes of 0.29 nm can be seen, corresponding to the {111} plane of aluminum, and lattice fringes in agreement with the spacing of the {101} plane of anatase structure.¹⁶⁾ There are also regions with different orientations of fringes, with mean size about 12 nm. From this observation, the TiO_2 film is considered to be finely crystalline with a mean crystal size of 12 nm. The Al_xO_y layer

Fig. 7 Morphology of X-TEM sample. (a) Optical micrograph and (b) bright-field TEM image.

Fig. 8 Results of EFTEM observation. (a) Zero-loss image, (b) Ti-L_{2,3}, (c) O-K and (d) Al-K elemental maps.

is amorphous like structure and approximately 5 nm thick. The interface between the TiO₂ and Al_xO_y could not be seen, nor can that between aluminum plate and Al_xO_y. It is considered that adhesion of these layers is consistently on the atomic scale. It is well known that aluminum plates have oxide layer on their surface and they are formed by the natural oxidation in the atmosphere or by anodic oxidation.^{17,18)} To confirm the formation of the oxide, the chemical composition

of the oxide layer was examined by XPS for an aluminum plate prepared by electrolytic polishing prior to sintering at 673 K. The XPS profile was obtained from the sample after natural oxide formation but before dipping. Al_{2p}, Al_{2s}, O_{1s} and O (KVV) were detected, and the ratio of Al to O calculated from the peaks in the XPS profile was about 0.67. This corresponds to a chemical composition of Al₂O₃. Therefore, Al₂O₃ layer in the coated samples appears to form during

Fig. 9 HRTEM image of interface between TiO_2 and Al plate for X-TEM sample.

electrolytic polishing or holding in atmosphere naturally prior to coating with TiO_2 precursor. And then, the oxide layer can be seen as the bright narrow area between the TiO_2 film and aluminum plate in the bright field image of the X-TEM sample. On semiconductor devices, the buffer layer between semiconductor materials and substrates is very important for the growth of superlattice layers on the substrate by relieving lattice mismatch between the two materials.¹⁹⁾ It has not been confirmed whether the TiO_2 film has the correct orientation relationship with substrate. It may be the case that the Al_2O_3 layer joins with aluminum plate continuously, and then, the TiO_2 layer also joins with an Al_2O_3 layer, which is the same kind of a metallic oxide as the TiO_2 , during sintering. This is supported by the good adhesion between these layers.

4. Conclusions

TiO_2 films were formed on aluminum plates by dipping in an advanced sol-gel solution. The effect of sintering conditions and lifting-up speed on photocatalytic activity of the films was investigated based on the change in UV absorption

with irradiation time. From X-ray diffraction and EFTEM analyses, the morphology and adhesion between the TiO_2 film and aluminum plate were characterized.

(1) The samples were confirmed to have photocatalytic activity, with optimal sintering temperature of 673 K and sintering time of 3.6 ks. The sintering conditions also correspond to the condition of anatase formation. The optimal sample exhibited a smooth surface, while other surfaces had scratches and peeling scars.

(2) The thickness of TiO_2 film was confirmed to be 30 nm by EFTEM. The interface between the TiO_2 film and aluminum plate was confirmed to be flat and free of cracks, and the adhesion between these two layers was found to be good.

(3) An unknown layer between the aluminum plate and TiO_2 film was assigned to aluminum oxide according to EFTEM and XPS analyses. As Ti was not detected in the aluminum plate, it is thought that the aluminum oxide layer suppresses diffusion of Ti atoms into the aluminum plate.

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