Effect of TiO2 thin film thickness and specific surface

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Effect of TiO$_2$ thin film thickness and specific surface area by low-pressure metal–organic chemical vapor deposition on photocatalytic activities

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Abstract

TiO$_2$ photocatalyst films having an anatase crystal structure with different thickness were prepared by the low-pressure metal–organic chemical vapor deposition (LPMOCVD) to examine the effect of growth conditions on photocatalytic activity. Film thickness was linearly proportional to the deposition time. Structure of the film was strongly dependent on the deposition time. In early stage of deposition, fine particles deposit on the substrate. As increasing the deposition time, crystal orientation is gradually selected following the Kolmogorov model and c-axis oriented columnar crystals become dominant. The photocatalytic activity strongly depends on the film deposition time (or film thickness) in nonlinear way. The optimum thickness of TiO$_2$ catalyst film grown by LPMOCVD may locate between 3 and 5 μm.
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Keywords: TiO$_2$ thin film; Low-pressure metal–organic chemical vapor deposition; Photocatalytic activity; Film thickness; Specific surface area

1. Introduction

Titanium dioxide (TiO$_2$), attracts much attention in recent years because of its unique physical and chemical properties, such as high refractive index, excellent optical transmittance in the visible and near-infrared regions, high dielectric constant and photocatalytic activity [1].

Recently, much attention has been paid to TiO$_2$ particles for cleaning the environment by photocatalytic decomposition of waste materials, pollutants [2–6] and harmful bacteria [7,8]. In many photodecomposition reaction systems, TiO$_2$ powders are often used as a photocatalyst. However, such powder catalysts causes several problems, such as [9,10] (1) difficulties in separation of the catalyst from suspension after the reaction, (2) difficulties in

prevention of aggregation in high concentration suspensions. To avoid such agglomeration, suspension must be diluted. Then the overall reaction rates tend to be slow. On the one hand, these problems can be solved by the use of immobilized (i.e., coated) catalyst particles. However, the coated catalysts are easily detached from the supports. To avoid these problems, TiO$_2$ thin films have recently been prepared by the sol–gel method [11,12] and chemical vapor deposition (CVD) method and applied to various reactions [13–15].

Since the mechanical and electrical properties of TiO$_2$ films are dependent on their composition, crystallinity, surface morphology and total surface area. Those strongly depend on the operation conditions of the CVD growth process. Then, it is important to control CVD conditions to optimize these characteristics. Many studies on the preparation of TiO$_2$ thin films by CVD methods have been reported but most of them focused on the relations between

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CVD process conditions and physical, chemical and electrical characteristics of TiO$_2$ thin films [16,17] but only few papers focused on the catalytic activity [18,19].

TiO$_2$ thin film photocatalysts have been applied for environmental applications such as air and wastewater treatment and deodorizers because of its large specific surface area, strong oxidizing powder, high photocatalytic activity, self-cleaning function and bactericidal and detox- ification activities [20–22]. The specific surface area significantly affects the photocatalytic activity [23,24] since the photocatalytic reactions occur on the surface where electrons and holes are produced under UV irradiation and also pollutants adsorb and dissociate. Thus, it is important to evaluate the effect of specific surface area on photocatalytic activities. Preparation by CVD is expected to provide larger specific surface area compared with other methods. In our previous paper [19], we reported that the photocatalytic activities of the TiO$_2$ film prepared by CVD were distinguished than sol–gel method because of its large specific surface area.

In this paper, we prepared TiO$_2$ photocatalyst films with an anatase crystal structure with different thickness by LPMOCVD and determined the effect of TiO$_2$ film thickness and specific surface area on photocatalytic activity. Also, we have investigated the change of TiO$_2$ film prepared by CVD method during growth process.

2. Experimental

2.1. Preparation of TiO$_2$ photocatalyst

TiO$_2$ photocatalyst films were grown on alumina balls (8 mm of diameter) by a LPMOCVD apparatus using titanium tetraisopropoxide (Ti[OCH(CH$_3$)$_2$]$_4$, TTIP) as a reagent. Detail of the reactor was described in our previous paper [19]. Argon gas was passed through a bubbler containing liquid TTIP, heated at 323 K, to carry the vapor to the reactor. The gas was further diluted with argon and oxygen at the inlet of the reactor tube. Mass-flow controllers modulated the flow rates of argon and oxygen gases. The system was evacuated by a rotary oil vacuum pump and the operating pressure was measured by a pressure transducer at the outlet of the reactor tube. LPMOCVD condition used for the preparation of TiO$_2$ films was such; total flow rate of gas fed to the reactor was 1500 sccm, oxygen concentration in the gas phase 50 mol%, operating pressure 1 Torr, reaction temperature 773 K. Surface morphology of the films grown on quartz glass substrate (20 mm × 20 mm) was evaluated using a field emission-scanning electron microscope (Hitachi, S-4700).

2.2. Evaluation of photocatalytic activity

Fig. 1 shows the annular tube type photoreactor used in this study. The photocatalyst balls were filled into the
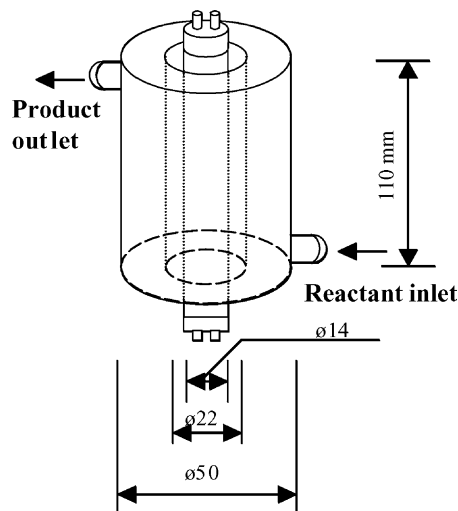

Fig. 1. Schematic diagram of annular tube type photoreactor.

annulus space of this reactor. A UV-A lamp (Philips, TL4W/ 05, with the most intensive power at 365 nm) was used as a source. To conduct re-circulating flow experiments, methy- lene blue solution of 500 cm^3 was prepared and circulated with a flow rate of 50 cm^3/min using a roller pump. Decomposition rate was evaluated from the change of methylene blue concentration at the reactor outlet as a function of irradiation time. The concentration of methylene blue was measured by the absorbance at $\lambda = 580$ nm, using a spectrophotometer (UV-1601, Shimadzu).

3. Results and discussion

3.1. Crystal morphology change with deposition time

Fig. 2 shows thickness of TiO$_2$ films prepared by LPMOCVD as a function of deposition time (τ_g). The thickness of TiO$_2$ film is almost linearly proportional to CVD reaction time. In our previous paper [19], we reported
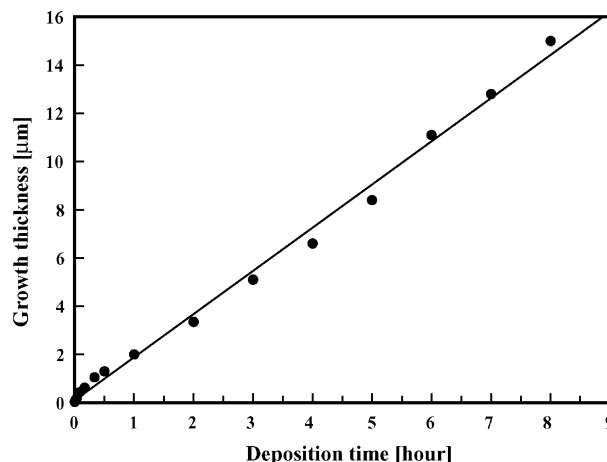

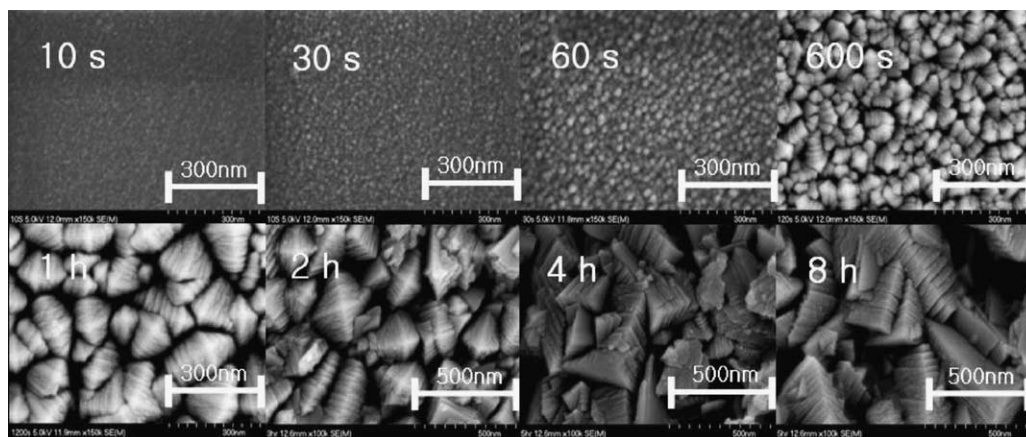Fig. 2. Thickness of TiO$_2$ film as a function of deposition time.

Fig. 3. Surface morphology (top view) of TiO$_2$ films grown by LPMOCVD at different deposition times.

that the XRD analysis of the TiO$_2$ films grown at 773 K indicated anatase type crystal structure. Also we reported that the growth rate increased linearly proportional to the feed rate of TTIP, but the crystal structure and orientation were unchanged. However, too much supply of TTIP caused decrease of growth rate via producing fine powders in the gas phase. Characterization of the grown film by EDX, ESCA and FT-IR indicated that the purity of the film was good.

Fig. 3 shows the surface morphologies of TiO$_2$ film at different deposition time. When the deposition time was short (τ_g = 10–60 s), very fine particles were observed. As the deposition time increased, the number density and the size of TiO$_2$ particles increased. After long deposition time (τ_g = 1–8 h) very densely packed columnar crystals with a prismatic top structure became dominant. However, after τ_g = 4 h, we did not see any significant change in the diameter of the crystals, i.e., only the thickness was increased. These result suggest that the specific surface area increased significantly in the early stage of TiO$_2$ film growth, however, the specific surface area may have been maintained almost constant after τ_g = 4 h.

Fig. 4 shows a cross-sectional TEM view of TiO$_2$ film grown on a SiO$_2$ substrate at τ_g = 10 s. For the observation, TiO$_2$ film was coated by 5 µm-thick Au layer. This indicates that this TiO$_2$ film of 30 nm in thickness is made of coagulated fine particles with random orientations.

Fig. 5 shows cross-sectional FE-SEM views of films after τ_g = 2 h (a) and 8 h (b). At τ_g = 2 h, total film thickness was 3.5 µm. In the bottom part, small particular crystals can be observed. On top of these particles, small columnar crystals grow and increase their sizes. At τ_g = 8 h, total film thickness increased up to 15 µm. This figure shows that the diameter of the columnar crystals are maintained almost constant at $d > 2$ µm. This result suggests that the specific surface area did not increase any more when columnar TiO$_2$ crystals with a uniform width grew after TiO$_2$ film grew thicker than 2 µm (i.e., $\tau_g > 2$ h).

Fig. 6 shows microstructural changes during TiO$_2$ film growth. These changes may correspond to Kolmogorov's "geometrical selection" of crystals [25].

3.2. Photocatalytic activity

In this study, the photocatalytic activity of TiO$_2$ films was evaluated by the photocatalytic decomposition of methylene blue in its aqueous solution. Fig. 7 shows plots of composition of methylene blue at the outlet of the reactor as a function of irradiation time, for TiO$_2$ coated catalyst balls prepared with different CVD deposition times. Initial concentration of methylene blue was about 8.6×10^{-6} mol/l and 500 cm^3 of solution was circulated into the reactor by a flow rate of 200 cc/min. These results indicate that methylene blue was decomposed by a photocatalytic reaction in presence of TiO$_2$ catalyst. A pseudo first-order kinetics with respect to methylene blue concentration can fit

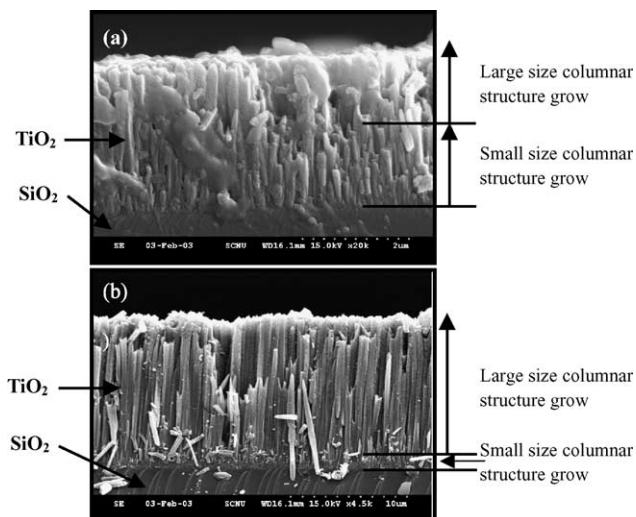Fig. 4. Cross-sectional TEM photo of TiO$_2$ film grown by LPMOCVD for τ_g = 10 s.

Fig. 5. Cross-sectional FE-SEM micrographs of TiO$_2$ film grown by LPMOCVD. Deposition time: (a) $\tau_g = 2$ h, (b) $\tau_g = 8$ h.

the experimental data of methylene blue photodegradation [26]

$$C = C_0 \exp(-kt) \qquad (1)$$

in which C is the methylene blue concentration at time t, C_0 the initial value and k the pseudo first-order rate constant. The slopes of the lines in Fig. 7 were determined by regression analysis and are given the k values in Table 1. The decomposition rate constant k is largest with catalyst balls of $\tau_g = 8$ h ($d = 15$ μm) and smallest with catalyst balls of $\tau_g = 1$ min ($d = 0.11$ μm). As the deposition time increased (or the thickness of TiO$_2$ film increased), the decomposition of methylene blue occurred faster, suggesting that the photocatalytic activity increased as the deposition time increased (or the thickness of TiO$_2$ film increased). However, Fig. 8 indicates that the catalytic activity depends nonlinearly on the film thickness, i.e., the activity increases drastically between $\tau_g = 0.5$ and 3 h (i.e., film thickness
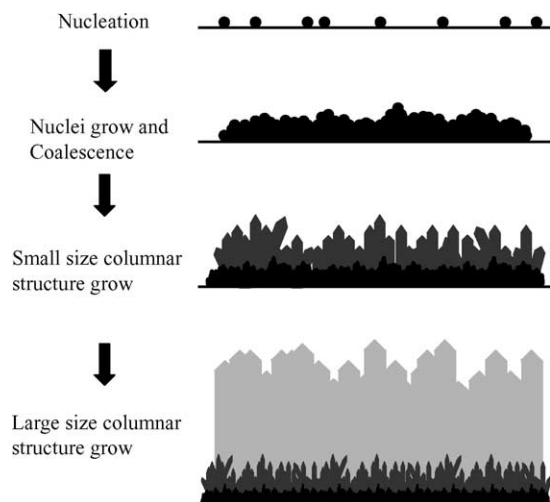

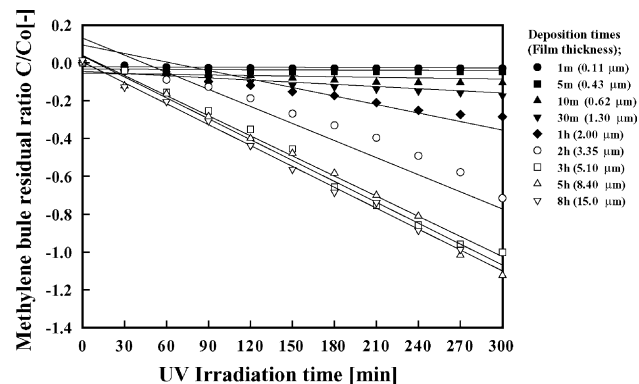Fig. 6. Morphological changes during LPMOCVD of TiO$_2$ film from TTIP.

Fig. 7. Effect of film thickness on decomposition of methylene blue in the early period of irradiation time.

Table 1
Degradation rates for methylene blue solution at different deposition times

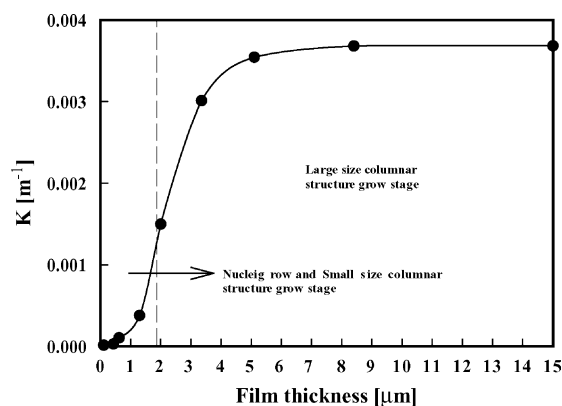| Deposition times (min, h)	Film thickness (μm)	k (min^{-1})
1 min	0.11	0.000017
6 min	0.43	0.000030
10 min	0.62	0.000105
30 min	1.30	0.000379
1 h	2.00	0.001499
2 h	3.35	0.003013
3 h	5.10	0.003545
6 h	8.40	0.003683
8 h	15.0	0.003685

Fig. 8. Effect of film thickness on the apparent first-order rate constant k.

between $d = 1$ and 5 μm). No distinguishable change in catalytic activity was observed for TiO$_2$ films thicker than 5 μm.

4. Conclusion

We obtained the following conclusions after synthesizing TiO$_2$ photocatalyst film with an anatase crystal structure by a LPMOCVD method using TTIP as a reagent. By the LPCVD with different deposition times, the film thickness and crystal morphology was controlled. Film thickness was linearly proportional to the deposition time. Structure of the

film was strongly dependent on the deposition time. In early stage of deposition, fine particles deposit on the substrate. As increasing the deposition time, crystal orientation is gradually selected following the Kolmogorov model and c-axis oriented columnar crystals become dominant. The photocatalytic activity strongly depends on the film deposition time (or film thickness) in nonlinear way. Catalytic activity increases drastically between $d = 1$ and 5 μm. In this thickness region, the columnar crystal structure with c-axis orientation with an almost constant diameter becomes dominant. The photocatalytic activity was not increased for the thicker film growth (5–15 μm). Thus, the optimum thickness of TiO_2 catalyst film grown by LPMOCVD may locate between 3 and 5 μm.

Acknowledgment

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