

## Preparation, Crystal Structure, and Photocatalytic Activity of TiO<sub>2</sub> Films by Chemical Vapor Deposition

Sang-Chul Jung<sup>†</sup> and Nobuyuki Imaishi\*

Dept. of Environmental Engineering, Sunchon National University,  
315 Maegok-Dong, Sunchon, Chonnam 540-742, Korea

\*Institute of Advanced Material Study, Kyushu University, 6-1 Kasuga-Koen, Kasuga 816-8580, Japan  
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**Abstract**—Photocatalytic activities of TiO<sub>2</sub> films were experimentally studied. TiO<sub>2</sub> films with different crystal structures (amorphous, anatase, rutile) were prepared by a Low Pressure Metal Organic Chemical Vapor Deposition (LPMOCVD) at different reaction temperatures and also by a Sol-Gel method using TTIP (Titanium Tetra Iso-Propoxyde). The Effect of CVD preparation method, CVD reaction conditions, crystal structure and wave-length of UV light on the photocatalytic decomposition rate of methylene blue in aqueous solution were studied. First, the characteristics of CVD preparation of TiO<sub>2</sub> films, such as the CVD film growth rate, crystal structure and morphology of the grown TiO<sub>2</sub> films, were experimentally studied as a function of CVD reaction temperature. Secondly, photocatalytic activities of TiO<sub>2</sub> films were evaluated by using two types of photo-reactors. The results indicated that TiO<sub>2</sub> films prepared by CVD exhibit higher photocatalytic activity than a catalyst prepared by the Sol-Gel method. Among the CVD grown TiO<sub>2</sub> films, anatase and rutile showed high photocatalytic activities. However, amorphous TiO<sub>2</sub> films showed lower activities. The activity of the photocatalysts of anatase films was excellent under all types of UV-lamps. The activity of CVD-prepared anatase films was four to seven times higher than that of photocatalyst films prepared by the Sol-Gel method.

Key words: TiO<sub>2</sub>, Chemical Vapor Deposition, Sol-Gel Method, Crystal Structure, Photocatalytic Activity

### INTRODUCTION

In 1972, Fujishima and Honda discovered the photocatalytic decomposition of water on TiO<sub>2</sub> electrodes. Since then, extensive research efforts have been conducted to understand the fundamental reaction mechanisms and to improve the photocatalytic efficiency [Fox and Dulay, 1993; Linsebigler et al., 1995] in the fields of hydrogen resource development and energy storage. In recent years, the most active research area of heterogeneous photocatalysis is its application to the environmental cleanup [Lozano et al., 1992; Palmisano et al., 1993; Milis et al., 1994]. This is inspired by the reports on the total destruction of organic compounds in polluted air and wastewater [Jacoby et al., 1995; Nimlos et al., 1996; Blanco et al., 1996; Terzian et al., 1991; Amadelli et al., 1991; Muszkat et al., 1992].

Recently, many researchers have been interested in the effect of the preparation method of TiO<sub>2</sub> catalyst on its photocatalytic activity [Konenkamp et al., 1993; Kim and Anderson, 1994; Tada and Honda, 1995]. A number of preparation techniques have been reported for TiO<sub>2</sub> thin films, such as thermal oxidation, sputtering, pyrolysis, sol-gel method and chemical vapor deposition (CVD). Among these, CVD is considered as a promising method to prepare high-quality thin films over large surface area with a well-controlled composition and low defect density [Kirkbir and Komiyama, 1987; Siefert et al., 1990; Egashira et al., 1994; Kim et al., 1998].

Photocatalytic chemical reactions on the surface of semiconduc-

tor materials are accompanied by multiple rate processes, starting from the absorption of light and ending with photo-generated electrons and holes on the surface. Since the mechanical and electrical properties of TiO<sub>2</sub> film depend on its thickness, composition, crystallinity and morphology [Tanaka et al., 1991; Tsai et al., 1997], it is important to control CVD conditions to optimize these characteristics during the CVD film-growth. In the research TiO<sub>2</sub> films via a Low Pressure Metal Organic CVD (LPMOCVD) were prepared by using titanium tetraisopropoxide (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>; TTIP hereafter) to study the effects of CVD operating conditions on the characteristics of the grown TiO<sub>2</sub> films and also on the photocatalytic activity for decomposition of methylene blue in its aqueous solution. The photocatalytic activities of CVD grown TiO<sub>2</sub> films were compared with those of TiO<sub>2</sub> films prepared by the Sol-Gel method.

### EXPERIMENTAL

#### 1. Preparation of TiO<sub>2</sub> Film by Chemical Vapor Deposition

CVD-grown TiO<sub>2</sub> films were prepared by using a horizontal hot-wall LPCVD apparatus shown in Fig. 1 with a large quartz reactor tube (47ΦID×50ΦOD, length 400 mm). Argon gas was passed through a bubbler containing TTIP liquid (Aldrich), heated at 323 K, to carry the vapor of TTIP to the reactor. The gas was further diluted with argon and oxygen at the inlet of the reactor tube. The flow rates of argon and oxygen gases were modulated by mass-flow controllers. The system was evacuated by a rotary oil vacuum pump, and the operating pressure was measured by a pressure transducer (Pirani 945, MKS, Ltd.) at the outlet of the reactor tube. The gas lines were heated to prevent the condensation of TTIP vapor in pipes. A porous

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: jsc@sunchon.ac.kr

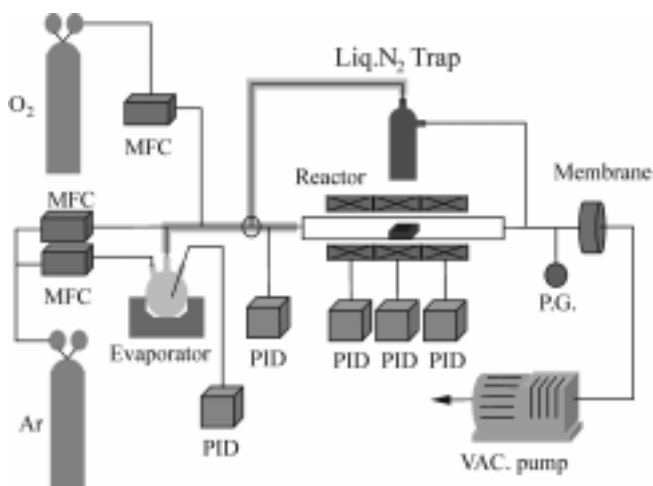


Fig. 1. Schematics of the LPMOCVD apparatus.

membrane with about 10  $\mu\text{m}$  pores (Fluoropore: FP1000, Sumitomo Electric Industries, Ltd.) was used to collect fine particles. The source gas was led to a liquid nitrogen trap, during the periods in which the reactor was heated to a desired temperature before the film growth and was cooled down to room temperature after CVD growth.

The crystal structure was characterized by X-ray diffraction (Max Science, MPX3). The morphology and the step coverage of the grown film were observed by using a scanning electron microscope (Hitachi, S-3500N). The films were characterized by a Fourier transform infrared spectrometer (Shimadzu, 8700).

## 2. Preparation of $\text{TiO}_2$ Photocatalyst

Photocatalysts were prepared by depositing  $\text{TiO}_2$  film (thickness: 2–5  $\mu\text{m}$ ) on alumina balls (Nikkato, HD-11,  $\Phi 8$  mm). Alumina balls were placed on a ball-holder plate and installed in the CVD reactor as shown in Fig. 2.

Following conditions were used for CVD operations: total flow rate 1,500 sccm, oxygen concentration in the gas phase 50 mol%, operating pressure 1 Torr, reaction temperature 423–1,173 K, TTIP evaporator temperature 323 K, reaction time 3–15 hr. The thickness of the grown  $\text{TiO}_2$  film was evaluated by measuring the weight change of small silica substrates placed at several spots on the ball-holder

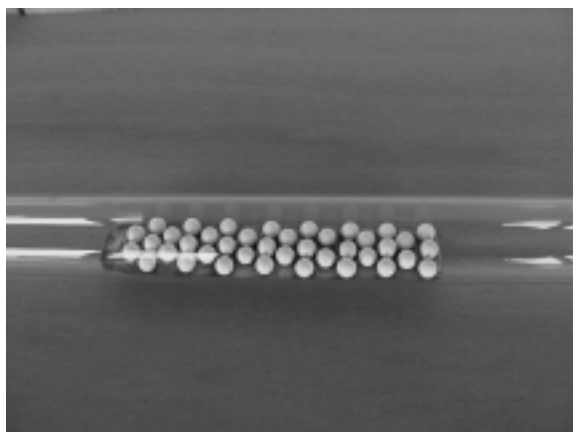


Fig. 2. Photographs of the alumina balls set in the quartz reactor tube.

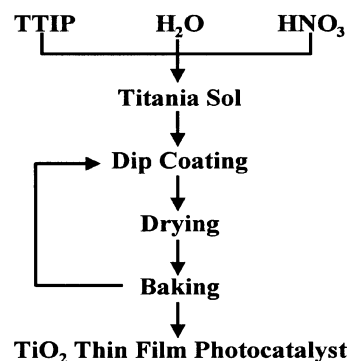


Fig. 3. Preparation of  $\text{TiO}_2$  film by the Sol-Gel method.

plate. Crystallinity was evaluated by XRD spectra of these CVD films grown on silicon substrates.

For the sake of comparison,  $\text{TiO}_2$  films were also prepared by the Sol-gel method.  $\text{TiO}_2$  Sol was prepared by using  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$  and TTIP. A solution with a ratio of 150 ml of  $\text{H}_2\text{O}$ : 15 ml of TTIP: 1 ml of  $\text{HNO}_3$  was refluxed at 353 K for 1 day. The precursor solutions were transparent and were very stable in air.  $\text{TiO}_2$  film was coated on rod substrates by the procedure indicated in Fig. 3. A three-step process of dipping, drying, and heat-treatment was used to coat the alumina balls. The film was dried in air and heat-treated in an electric furnace at 773 K for 24 hr to obtain anatase film on catalyst balls.

## 3. Evaluation of Photocatalytic Activity

Fig. 4 shows the annular tube type small photo-reactor used in this study. The annulus space of this reactor was filled with the CVD photocatalyst balls prepared at various temperatures. Two types of experiments were conducted. In the first case, an aqueous solution of methylene blue (total volume: 500 cc) was circulated at a constant flow rate of 50 cc/min using a roller pump (RP-1000, EYELA). Decomposition rate was evaluated from the change of concentration of methylene blue at the reactor outlet with reaction times. In the second case, the solution was fed to the reactor without re-circulation (single pass operation).

Fig. 5 shows schematics of a larger scale reactor with double annulus channel structure. Thermostated water was fed to the outer-

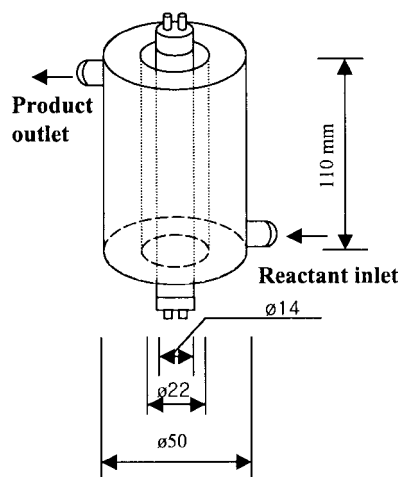


Fig. 4. Schematic diagram of annular tube type photo-reactor.

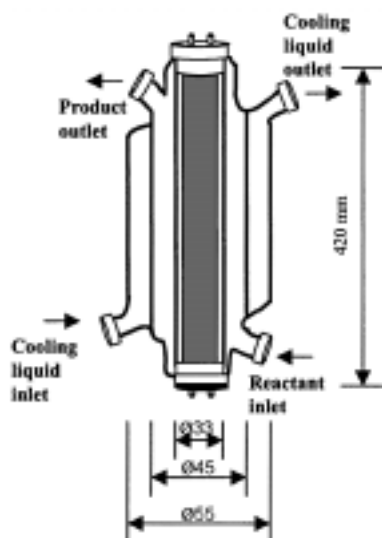


Fig. 5. Schematic diagram of triple annular type photo-reactor.

most channel to maintain the reaction temperature. To conduct re-circulating flow experiments, methylene blue solution of 1,000 cm<sup>3</sup> was prepared and circulated with a flow rate of 200 cm<sup>3</sup>/min. In all cases, concentration of methylene blue was measured by the absorbance at  $\lambda=580$  nm, using a spectrophotometer (UV-1601, Shimadzu). Dependency of the photocatalytic activity of catalysts preparation method was evaluated by using these reactors under different UV source.

To evaluate the effect of UV light wave length, three kinds of UV sources were used; UV-A [Philips, TL4W/05 and F15T8BLB: (the most intensive wavelength; 368 nm)], UV-B [Sankyo Denki, G4T5E and G15T8E: (the most intensive wavelength; 305 nm)] and UV-C [Philips, TUV4W/G5 and TUV15W/G15T8: (the most intensive wavelength; 250 nm)]. Under an irradiation of UV-C lamp, methylene blue was slowly decomposed through a homogeneous photo reaction, even without the photocatalyst balls. However, under an irradiation of UV-A lamp, no decomposition occurs without photocatalyst balls. Among the experimental results in the following

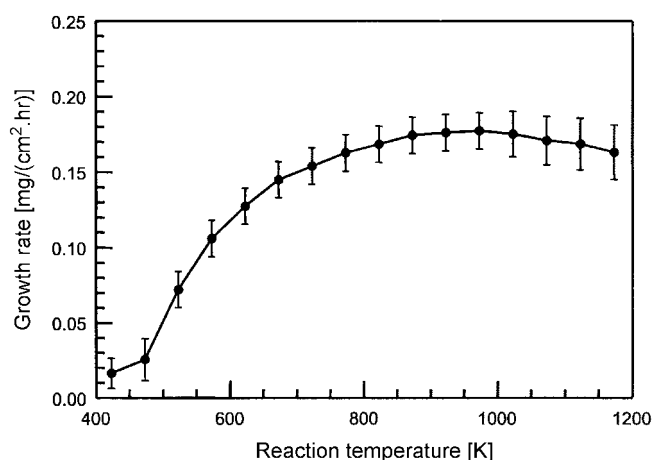


Fig. 6. Growth rate of TiO<sub>2</sub> film by LPMOCVD using TTIP. CVD growth conditions: Total pressure; 1 Torr, total flow rate; 1,500 sccm, oxygen concentration; 50 mol%.

sections, the photocatalytic activities of TiO<sub>2</sub> films are most precisely represented by the experimental results with UV-A lamp.

## RESULTS AND DISCUSSION

### 1. Characterization of TiO<sub>2</sub> Films Prepared by LPMOCVD

Growth rate of TiO<sub>2</sub> depends on the CVD reaction temperature as shown in Fig. 6. Growth rate was very low at low reaction temperatures, 423 K and 473 K. As the reaction temperature increases, the growth rate also increases. And the growth rate decreases at above 973 K. This decrease was caused by the powder formation in the reactor, because the amount of particles collected in the membrane filter at the outlet increased steeply at above 973 K.

X-ray diffraction patterns of the TiO<sub>2</sub> films grown on silica substrates under different reaction temperatures are shown in Fig. 7. The diffraction patterns indicate that amorphous TiO<sub>2</sub> films were grown under CVD reaction temperature range of 423–473 K. Ana-

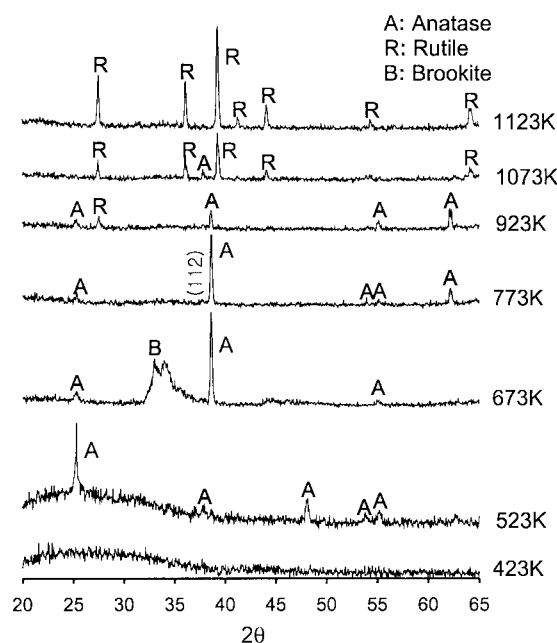


Fig. 7. X-ray diffraction pattern of the TiO<sub>2</sub> films grown at 1 Torr under different temperatures.

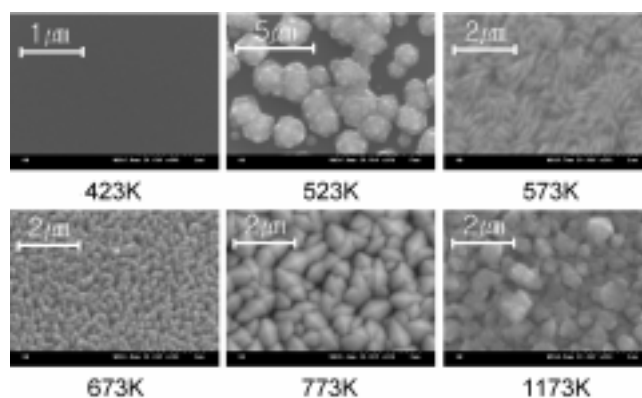


Fig. 8. Surface morphology of TiO<sub>2</sub> films grown by CVD at 1 Torr under various temperatures (SEM observation).

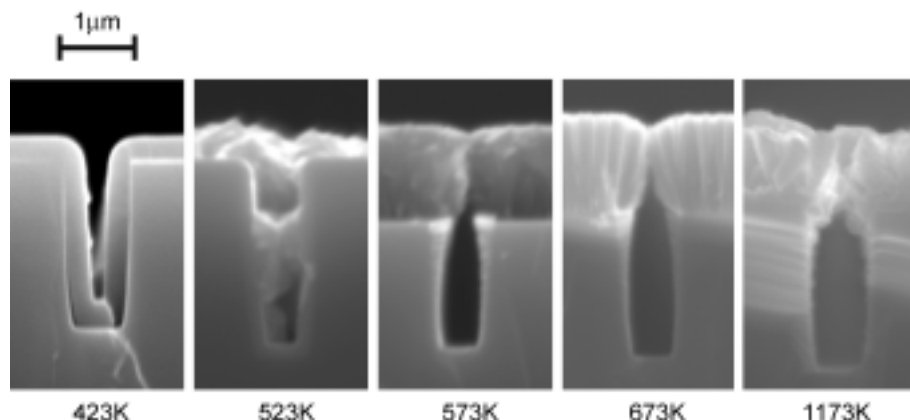


Fig. 9. SEM photos of grown  $\text{TiO}_2$  film profile on micro-scale trench at various CVD temperatures.

tase films were grown at 523–923 K. However, a weak peak of brookite was observed at 673 K. Peaks of rutile began to appear at 923 K.  $\text{TiO}_2$  films prepared at 1,073 K still indicate a weak peak of anatase. Films grown at 1,123 K indicate XRD peaks of rutile.  $\text{TiO}_2$  films prepared at 673 K and 773 K indicate XRD peaks of (112) oriented anatase. However, the effects of the growth temperature on crystal orientation are not clearly understood.

Fig. 8 shows SEM observation results of surface morphology of the  $\text{TiO}_2$  CVD films grown at various temperatures.  $\text{TiO}_2$  films grown at low temperatures (such as Fig. 7 at 423 K) are composed of very fine particles and show smooth and flat surfaces.  $\text{TiO}_2$  film grown at 523 K shows islands of anatase crystals in the amorphous film. At higher CVD temperatures, surface morphology of the grown  $\text{TiO}_2$  films changes as shown in Fig. 8.

Fig. 9 shows the experimentally observed step coverage of the  $\text{TiO}_2$  film grown at different CVD reaction temperatures.  $\text{TiO}_2$  films grown at 423 K and 523 K show a conformal step coverage (i.e., the film thickness on the top is the same as that at the bottom of the step). However,  $\text{TiO}_2$  films grown at higher temperatures (above 573 K) show a non-conformal step coverage. These different profiles indicate that the surface reaction rate constant ( $k_s = h\nu/4$ ) is strongly

dependent on the growth temperature, i.e., at lower temperatures,  $h$  is small and  $h$  approaches to unity at higher temperatures [Akiyama et al., 1995; Jung et al., 1999]. Where  $h$  is the reactive sticking

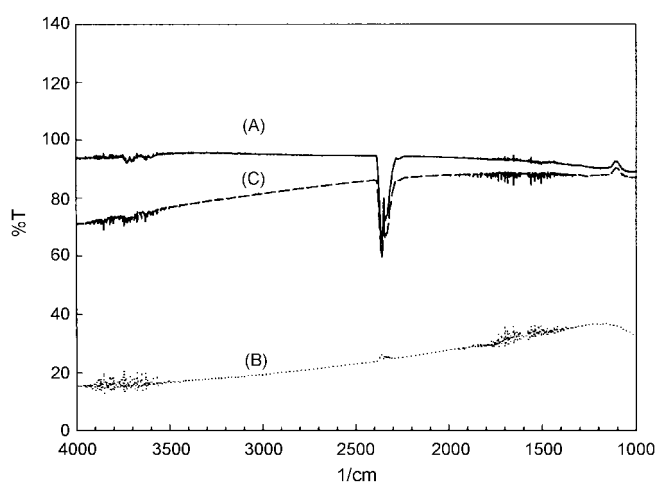


Fig. 10. Infrared spectrum of the  $\text{TiO}_2$  films grown by CVD at 1 Torr under various temperatures (A: 473 K, B: 773 K, C: 1,073 K).

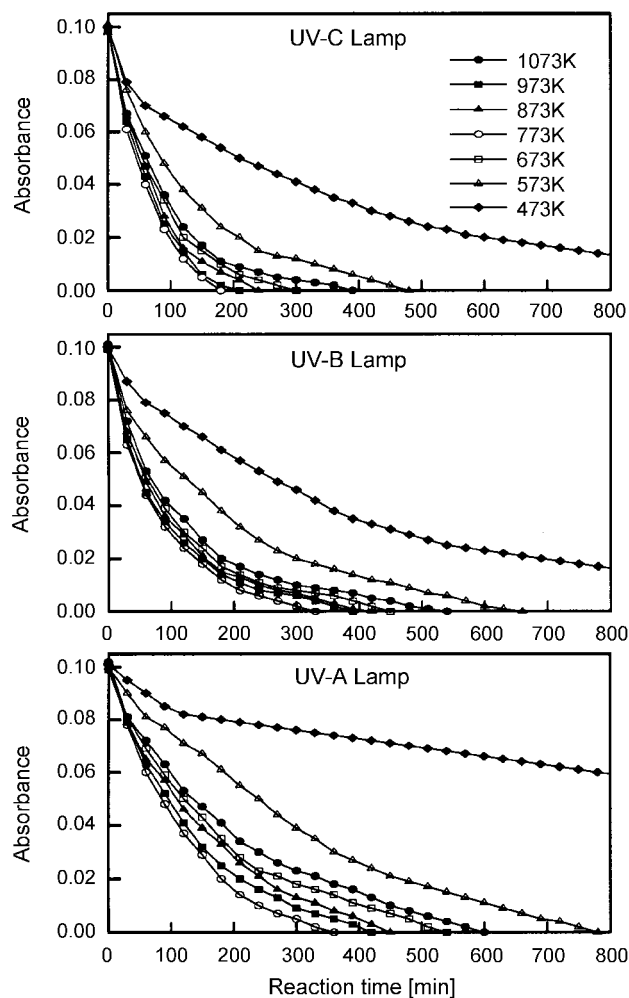


Fig. 11. Effect of CVD temperatures on photocatalytic activity of  $\text{TiO}_2$  films for decomposition of methylene blue in aqueous solution under three types of UV-lamp irradiation using a reactor of Fig. 4 (Re-circulating a 500 ml of solution with a flow rate of 50 cc/min).

coefficient and  $v = [8RT/(\pi M_A)]^{1/2}$  is the mean molecular velocity of A [m/s], R the gas constant [J/(mol·K)], T the temperature, and  $M_A$  the molecular weight of A.

Fig. 10 shows FT-IR spectrum of TiO<sub>2</sub> films prepared by CVD at different reaction temperatures. Organic group was not detected in all types of TiO<sub>2</sub> films (Fig. 10A: an amorphous film grown at 473 K, Fig. 10B: an anatase film grown at 773 K and Fig. 10C: a rutile film grown at 1,073 K). The absorption peaks at near 2,380 cm<sup>-1</sup> correspond to that of carbon dioxide adsorbed on TiO<sub>2</sub> surface in the air. These results indicate that TiO<sub>2</sub> films prepared by the present LPMOCVD reactor are considerably pure.

## 2. Photocatalytic Activity of TiO<sub>2</sub> Film Prepared by CVD

In this study, the photocatalytic activity of TiO<sub>2</sub> films was investigated with the photocatalytic decomposition of methylene blue in its aqueous solution. Methylene blue was chosen since it does not show strong absorption (and photo-decomposition) of UV light of UV-A lamp.

Fig. 11 shows the plots of methylene blue composition, at the outlet of the reactor of Fig. 4, as a function of irradiation time of different UV lamps with TiO<sub>2</sub> coated catalyst balls prepared at various CVD reaction temperatures. Initial concentration of methylene blue was about  $8.6 \times 10^{-6}$  mol/l and 500 cm<sup>3</sup> 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 the presence of TiO<sub>2</sub> catalyst and UV light. The decomposition rate is the largest under a UV-C lamp irradiation and the

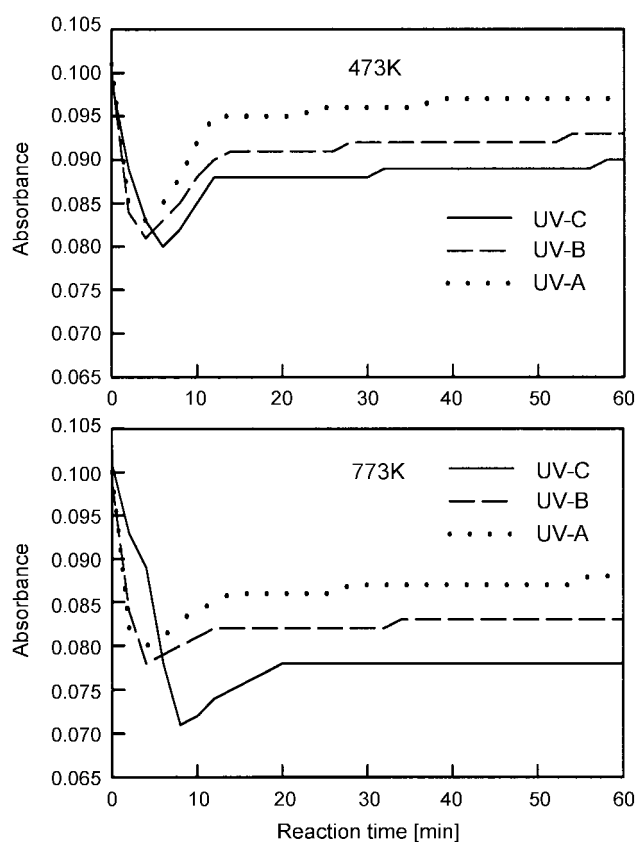


Fig. 12. Photocatalytic decomposition of methylene blue under one-pass flow condition using a reactor of Fig. 4 (Flow rate: 50 cc/min).

smallest under a UV-A lamp. The films prepared at 473 K showed the smallest activity. The activities of the photocatalysts of anatase (prepared by CVD at 673 K, 773 K, 873 K and 973 K) exhibit large activity under any type of UV lamp. Among them, the catalyst prepared at 773 K showed the highest activity. The rutile films prepared at 1,073 K were less active than anatase films (except for the anatase prepared at 573 K).

Fig. 12 shows time variations of the methylene blue concentration at the reactor exit of a photo-reactor (Fig. 4) during one-pass type operations. All results in Fig. 12 exhibit large initial decomposition rates. It is attributed to the fact that methylene blue was absorbed on the surface of catalyst balls. Gradually the mass transfer rate in liquid phase and photocatalytic reaction rate determines the decomposition rate.

## 3. Comparison of the Photocatalytic Activities of TiO<sub>2</sub> Films by CVD with Sol-Gel Method

Fig. 13 compares the decomposition rates of methylene blue with catalyst balls prepared by CVD at 773 K and that with catalyst balls prepared by the Sol-Gel method, using a large photo-reactor of Fig. 5. Decomposition rate was very high under the UV-C lamp and was lowest under the UV-A lamp. Under UV-A lamp light, the CVD photocatalyst took about 140 min to attain complete decomposition of methylene blue in 1,000 cm<sup>3</sup> of solution. On the contrary,

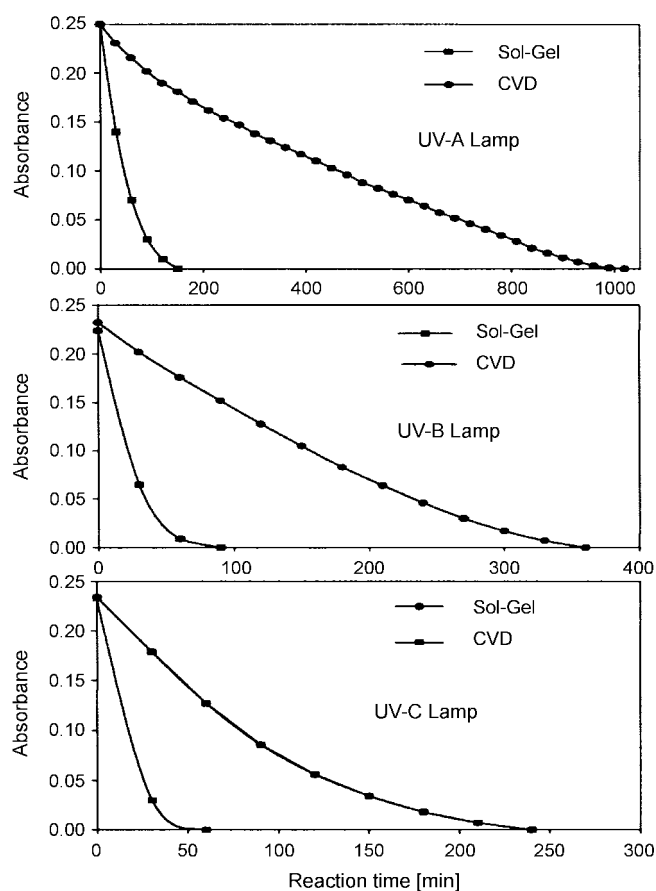


Fig. 13. Effect of the preparation method on the photocatalytic activities of TiO<sub>2</sub> films for decomposition of methylene blue in aqueous solution using the reactor in Fig. 5. Comparison between the Sol-Gel method and a CVD film grown at 773 K.

the Sol-Gel photocatalyst needed about 1,000 min. Under UV-B lamp light, the CVD photocatalyst took about 90 min and the Sol-Gel photocatalyst about 360 min. Under UV-C lamp light, CVD photocatalyst took about 40 min and Sol-Gel photocatalyst about 240 min. These results indicate that the activity of the CVD photocatalyst is higher than that of the Sol-Gel catalyst by a factor of 4 to 7.

## CONCLUSION

We studied the preparation of  $\text{TiO}_2$  photocatalyst films on alumina balls by LPMOCVD using TTIP. Amorphous films were obtained in the temperature range of 423–473 K. Anatase films were obtained at 523–923 K and rutile films at 1,073 K or above. Surface morphology of  $\text{TiO}_2$  film changes by increasing temperature, from very small grain particles to more well-defined large grain crystals. The difference in the step coverage profiles indicates that the CVD surface reaction rate increases with reaction temperature. The CVD grown  $\text{TiO}_2$  films were characterized as a high-quality from FT-IR spectra. The activity of photocatalyst films was evaluated by the decomposition rate of methylene blue in aqueous solution. The results indicate that CVD-grown anatase films exhibit excellent activity under all type of UV-lamps. The activity of the amorphous film was the lowest. Rutile films showed higher activity than that of an anatase grown at 573 K, but lower than those of other anatase films. The activity of CVD photocatalyst was higher than that of catalyst prepared by the Sol-Gel method by a factor of 4 to 7.

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