



## Crystallinity Effect on the Photocatalytic Performance of TiO<sub>2</sub> Thin Films Prepared by CVD Process

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### ABSTRACT

TiO<sub>2</sub> thin films were synthesized by using chemical vapor deposition (CVD) process at 530°C to examine the effect of CVD synthesis time on physical and optical properties, and photocatalytic activities. Thin films of nano-sized spherical TiO<sub>2</sub> particles were produced on borosilicate glass substrates by the CVD process for 60 min and 90 min. As the synthesizing time increased, the particle size of the TiO<sub>2</sub> films increased, but the thicknesses of the films decreased. The band gaps of the films prepared by deposition for 60 and 90 min were 3.51 and 3.25 eV, respectively. The photocatalytic activities of the TiO<sub>2</sub> thin films were monitored by studying the degradation of methylene blue under simulated solar light irradiation. The rate constant of methylene blue decomposition was found to increase from  $4 \times 10^{-4}$  to  $6 \times 10^{-4} \text{ min}^{-1}$  when increasing the synthesis time from 60 min to 90 min. We proposed that the crystallinity of TiO<sub>2</sub> films is the main factor to enhance photocatalytic efficiency.

### INTRODUCTION

Titanium dioxide (TiO<sub>2</sub>) has unique physical and chemical properties, such as high refractive index, high chemical stability, excellent optical transmittance in the UV and visible regions, and high photocatalytic activity [1,2]. Recently, TiO<sub>2</sub> photocatalysts have been used for decontaminating the organic compounds in wastewater and for their antibacterial effects [3,4]. In many photocatalysis reactions, TiO<sub>2</sub> powders are used as photocatalysts for decomposing harmful pollutants. However, the powder form of TiO<sub>2</sub> causes two main problems, namely (1) difficulties in reusing the catalyst due to the waste of a large amount of water, and (2) agglomeration of catalyst particles in high concentration suspensions. To overcome these issues, the immobilization of TiO<sub>2</sub> on transparent substrates was developed to facilitate photocatalytic purification of water contamination. The coating by thin films of photocatalysts on glass substrates is one of solutions. Photocatalysts in the form of thin films are more reusable than those in the form of particles. Therefore, TiO<sub>2</sub> thin films are more suitable in long-term applications. It has been shown that TiO<sub>2</sub> thin films can be prepared by various methods, such as the sol-gel method [5,6], electrophoretic deposition [7,8], spin coating [9,10], sputtering [11,12], and chemical vapor deposition (CVD) [13,14]. Among these methods, CVD has advantages because it is able to prepare a catalyst coated on various substrates (e.g. Al<sub>2</sub>O<sub>3</sub>, glass slide, FTO, and ITO),

with a high catalytic activity surface and low catalyst volume. Many studies on the preparation of TiO<sub>2</sub> thin films by CVD methods have been reported but most of them focused on the relations between CVD process conditions and physical, chemical, and electrical characteristics of the TiO<sub>2</sub> thin films [13-17], but studies on the effect of crystallinity on photocatalytic activity have been missing.

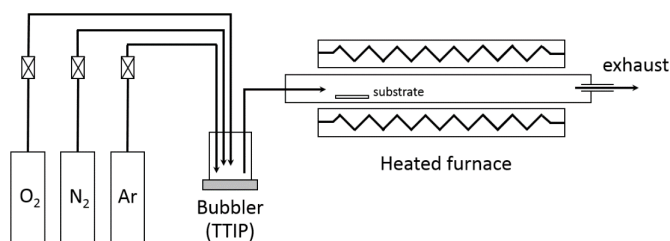
In this paper, we report on the synthesis and characterization of TiO<sub>2</sub> films prepared by using CVD for synthesis times of 60 min and 90 min. The physical and optical properties of the TiO<sub>2</sub> thin films were characterized by atomic force microscopy (AFM), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS), UV-Vis spectrophotometry and Raman spectroscopy. The photocatalytic activities of the TiO<sub>2</sub> thin films were evaluated by examining the photodegradation reaction of methylene blue (MB) under simulated solar light irradiation. We observed that the rate of decomposition is higher for the film deposited for a synthesis time of 90 min than that deposited for 60 min.

### METHODOLOGY

#### Preparation of TiO<sub>2</sub> films

The experimental setup of the CVD process for the synthesis of TiO<sub>2</sub> films on glass slides is shown in **Figure 1**. Firstly, titanium tetra isopropoxide (TTIP, Ti [OCH (CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, 97%, Sigma-Aldrich)

was used as the precursor for Ti. The 20 ml of TTIP was diluted in absolute ethanol (200 ml). Then, the TTIP was vaporized at 80 °C in a bubbler using argon gas. The volatilized TTIP solvent and the mixture of argon, oxygen and nitrogen gases were introduced into a quartz tube (100 cm length, I.D. = 4.4 mm), maintained at a constant temperature of 530°C for 60 or 90 min. The films synthesized for 60 and 90 min will be labeled as “60-min film” and “90-min film”, respectively. The temperature and time used to produce the TiO<sub>2</sub> films are within the optimum to produce transparent films without contamination from residual carbon. The flow rate of O<sub>2</sub>:N<sub>2</sub>:Ar was 500:55:200 sccm. Ar was used as a gas carrier. N<sub>2</sub> was used as an additional gas carrier producing extra thrust for bubbling the ethanol solution. The presence of O<sub>2</sub> can lower activation energy of TIPP dissociation for TiO<sub>2</sub> formation by ultrasonication [16-17]. The glass slides used as the substrates were pre-treated in ethanol for 30 min prior to the deposition step. Then, the glass slide was placed on an alumina boat located 30 cm away from the side of the tube where the gases entered.



**Figure 1** A schematic diagram of the CVD-coating of TiO<sub>2</sub>

### Characterization

The details of surface morphology and element composition were obtained using FE-SEM from JEOL JSM-6335F, EDS and AFM from a Nanoscope IIIa (Digital Instrument, USA). The transmittances and band gap of the two samples were obtained using a UV-vis spectrophotometer (Perkin Elmer Lambda 1050) at a wavelength of 300-700 nm. The crystalline phase of the TiO<sub>2</sub> thin film was determined using Raman spectroscopy with an excitation wavelength of 532 nm with a HORIBA Jobin-Yvon T64000 Raman spectrometer.

### Photocatalytic degradation of methylene blue

The photocatalytic performances of the two samples were evaluated by the photodegradation of methylene blue as the model

dye solution under simulated solar light irradiation. The 2 cm × 3 cm films of the photocatalyst were placed in a reactor with 100 mL of a 1.5 × 10<sup>-5</sup> M aqueous MB solution for one hour to reach an adsorption-desorption equilibrium before being subjected to illumination. A simulated solar illumination lamp (Halogen lamp 50 W, Philips) was used as a light source. Then, the reactor system was irradiated for 6 h with periodic measurements of the remaining solution (15 minute intervals). This monitoring proceeded by collecting 3 mL of the solution. The absorbance spectrum was measured and the solution was returned to the reactor. The concentrations of MB were estimated based on the absorbance at 664 nm. The percentage of dye degradation was calculated from the following equation:

$$\% \text{Degradation} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100,$$

where  $C_0$  is the initial concentration of dye and  $C_t$  is the concentration of dye after irradiation time  $t$ .

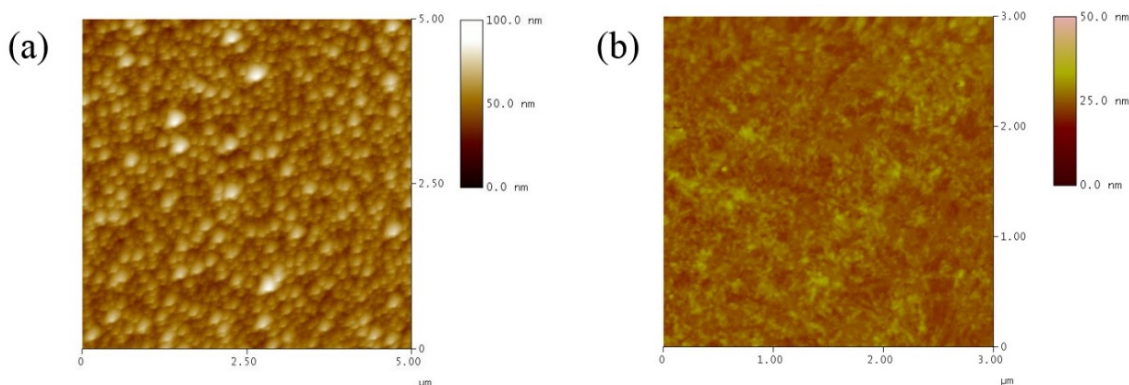
## RESULTS AND DISCUSSION

### Surface morphology

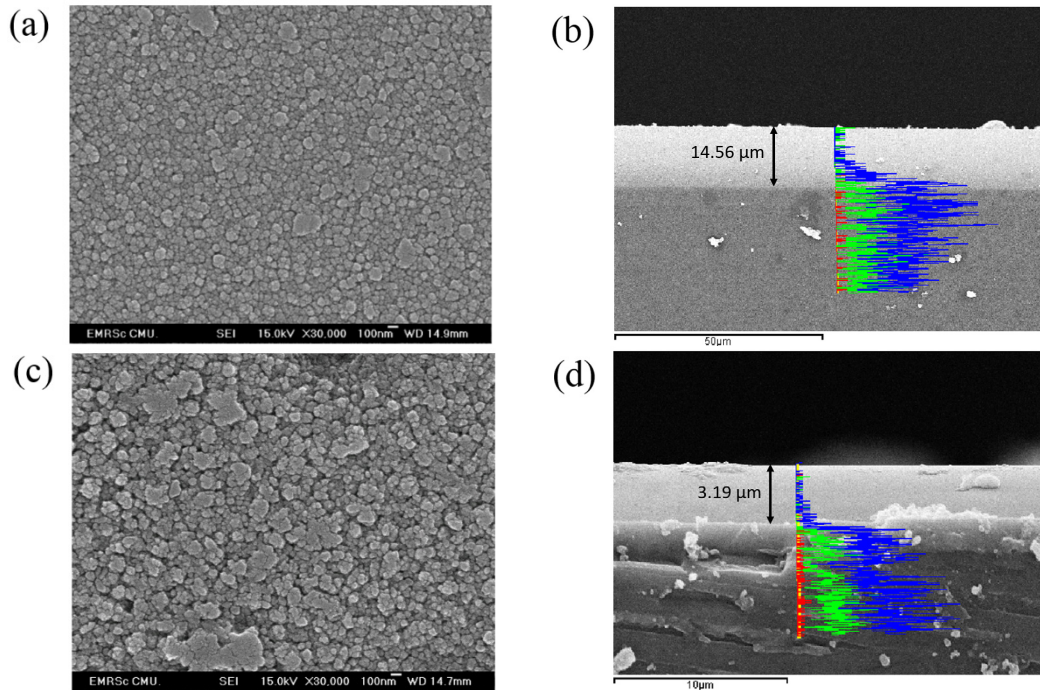
The surface topography of the 60-min and 90-min films was investigated by AFM as shown in **Figure 2(a)** and **2(b)**. The surface roughness of the 60-min and 90-min films was measured to be  $6.014 \pm 0.575$  and  $2.192 \pm 0.747$  nm, respectively. The particle size of the 60-min film was  $87.1 \pm 18.6$  nm. For the 90-min film, the AFM image can not distinguish particles in the film. The particle size for this film could not be determined. SEM morphological images of the TiO<sub>2</sub> films in **Figure 3(a)** and **3(c)** display the agglomeration of TiO<sub>2</sub> nanoparticles, forming the thin film TiO<sub>2</sub>. Estimated particle sizes of the 60-min and 90-min films are  $87.1 \pm 18.6$  and  $3.19 \pm 0.15$  nm, respectively. The cross section SEM images are also shown in **Figure 3**. The EDS line profiles are useful for distinguishing the region of the TiO<sub>2</sub> films from the glass substrates. The thicknesses of the 60-min and 90-min films were measured to be  $3.19 \pm 0.15$  and  $3.19 \pm 0.15$  μm, respectively. The particle size estimated from AFM is larger than that estimated from SEM because of the nature of tip movement during scanning.

### Raman Spectroscopy

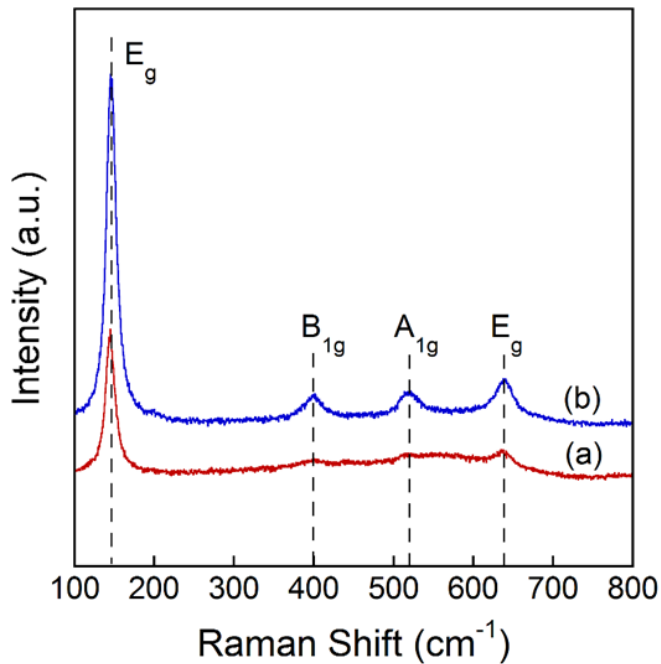
Raman spectroscopy was an important technique to examine the crystal phase of TiO<sub>2</sub> [18]. **Figure 4** shows the Raman spectra from



**Figure 2** AFM images of TiO<sub>2</sub> thin films synthesized at 530°C for (a) 60 min and (b) 90 min.

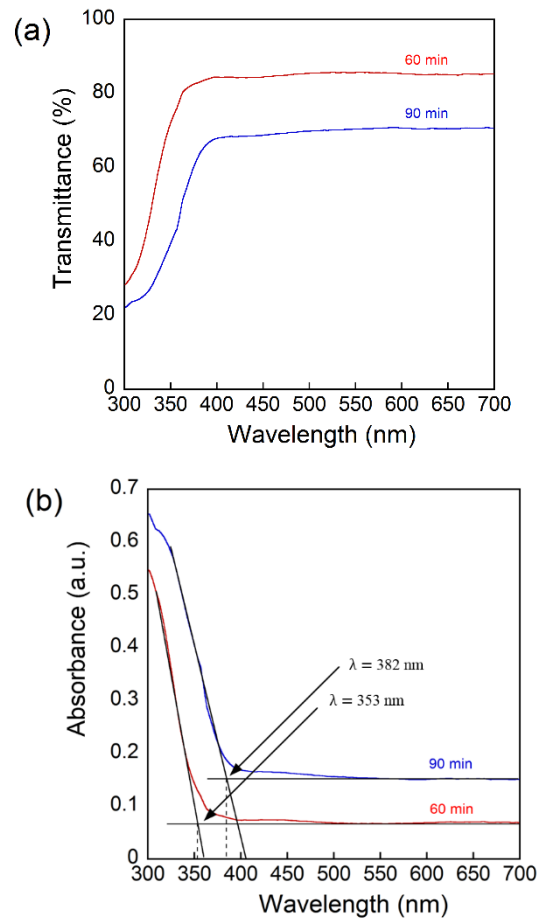


**Figure 3** SEM images of the surface and the cross section of  $\text{TiO}_2$  thin films synthesized at  $530^\circ\text{C}$  for 60 min (a, b) and for 90 min (c, d). EDS line profiles are shown in (c) and (d), where red is titanium, green is oxygen, and blue is silicon.



**Figure 4** Raman spectra of  $\text{TiO}_2$  thin films synthesized at  $530^\circ\text{C}$  for (a) 60 min and (b) 90 min.

the 60-min and 90-min films. The strong Raman peaks at around 145, 401, 521 and  $640\text{ cm}^{-1}$  in **Figure 4(b)** can be assigned to anatase  $\text{TiO}_2$  without rutile or brookite phases [19-20]. The weak-signal peaks in **Figure 4(a)** can be attributed to the non-well-crystallization of anatase  $\text{TiO}_2$ . The transmittance spectra of the 60-min and 90-min films are shown in **Figure 5(a)**. The absorption margins dramatically shift from 353 nm for the 60-min film to 382 nm for the 90-min film. The energy gap of  $\text{TiO}_2$  films can be calculated from the relation,



**Figure 5** (a) Transmittance and (b) absorbance of  $\text{TiO}_2$  thin films synthesized at  $530^\circ\text{C}$  for 60 and 90 min.

$E = hc/\lambda$  where  $h$  is the Planck constant,  $c$  is the speed of light, and  $\lambda$  is the cut-off wavelength in the plot of absorbance. The band gaps of the 60-min and 90-min films were calculated to be 3.51 eV and 3.25 eV, respectively.

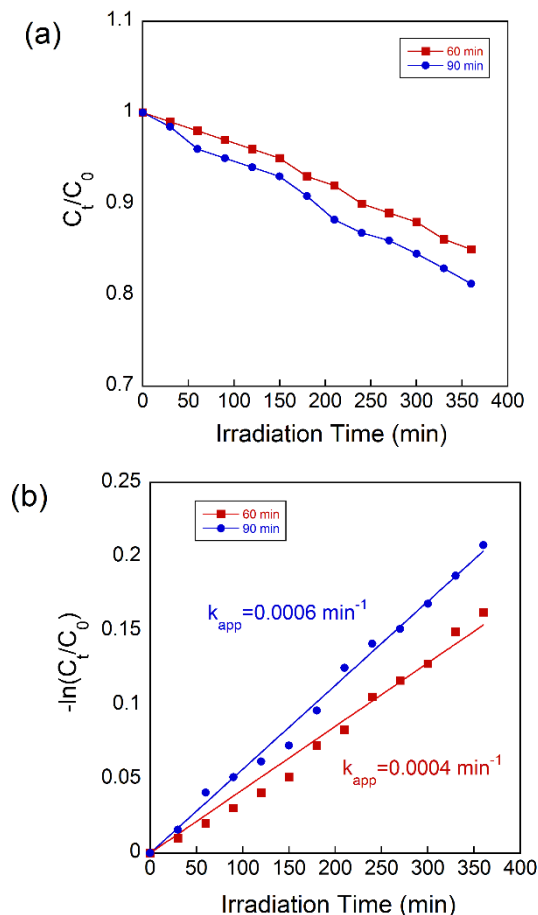
### Photocatalytic performances

The photodegradation of MB using the 60-min and 90-min films under simulated solar light irradiation is illustrated in **Figure 6(a)**. A slight decrease in MB concentration was observed in the presence of the 60-min and 90-min films. The methylene blue was degraded approximately 15% and 19% by the 60-min and 90-min films, respectively. It is notable that the 90-min film displays a better degradation effect than the 60-min film.

To quantitatively analyze the reaction kinetics of MB degradation, the experimental data in **Figure 6(a)** was fitted by the Langmuir–Hinshelwood model [21], as expressed by the following equation:  $-dC/dt = k_{app}t$ , where the  $C$  is the concentration and  $k_{app}$  is the apparent reaction rate constant. Integration of the above equation will lead to the concentration as a function of time:  $-\ln(C/C_0) = k_{app}t$ . Using such kinetic analysis, it is evident that the photocatalytic degradation of MB follows the pseudo-first order kinetic shown in **Figure 6(b)**. From the linear fitting curves of  $-\ln(C/C_0)$  versus irradiation time,  $t$ , the MB degradation rate constants  $k_{app}$  were extracted to be  $4.0 \times 10^{-4}$  and  $6.0 \times 10^{-4} \text{ min}^{-1}$  for the 60-min and 90 min films, respectively. The 90-min film exhibited the higher value of  $k_{app}$  than the 60-min film.

### Discussion

The decrease of  $\text{TiO}_2$  film thickness with increasing operating time likely attributes to the agglomeration of the particles in the  $\text{TiO}_2$  films. In addition, the impurity atoms of Si and/or B from borosilicate glass might diffuse into  $\text{TiO}_2$  films at the high temperature of  $530^\circ\text{C}$ . The amount of the impurity atoms in  $\text{TiO}_2$  films are very small. Thus, their effect on optical and chemical properties of the films would be limited. Therefore, the quantum size effect and crystallinity of the  $\text{TiO}_2$  films would mainly contribute to the deviation in band gap between 60-min  $\text{TiO}_2$  and 90-min  $\text{TiO}_2$  films. The large band gap in 60-min  $\text{TiO}_2$  film can suppress the recombination rate for the photogenerated electron-hole pairs and enhance photocatalytic performance of the  $\text{TiO}_2$  films. However, the 60-min film displayed less degradation of MB, reflected in a lower apparent reaction rate. This inconsistency can be explained by considering crystallinity of the film [18]. According to the results of Raman spectroscopy, the prominent peaks of the 90-min film have higher signal-to-noise than the 60-min film. This indicates a better crystallinity in the film synthesized for the longer time. Furthermore, the anatase-phase  $\text{TiO}_2$  is the most efficient phase of  $\text{TiO}_2$  for MB degradation under simulated solar light irradiation [22–23]. We suggest that the effects of completeness are the main factors for the difference in photodegradation efficiency of MB solutions. From the SEM images, the thickness of the 60-min film is larger than that of the 90-min film. In contrast, the particle size of the 60-min film is smaller than that of the 90-min film. This can be understood by the agglomeration of particles at the longer synthesizing time. The contradiction of film thickness between the 60-min and 90-min films can be explained by the decrease of TTIP concentrations during the bubbling process. The amount of visible white vapor flowing into the quartz tube for the 90-min films was less than the initial deposition for the 60-min films. This could be a reason for the reduction of the



**Figure 6** (a) Photodegradation efficiencies of MB solution as a function of irradiation time and (b) pseudo-first-order reaction kinetic ( $-\ln(C/C_0)$ ) versus irradiation time in the presence of MB photolysis,  $\text{TiO}_2$  (60 min, red square), and  $\text{TiO}_2$  (90 min, blue circle) prepared by CVD process at  $530^\circ\text{C}$ .

90-min film thickness.

The thickness of the 60-min and 90-min films was 14.56 and 3.19  $\mu\text{m}$ , respectively, while the energy band gap of these was 3.51 and 3.25 eV. The relation of an increase of band gap with a decrease of film thickness has not been reported in  $\text{TiO}_2$  films prepared by sol-gel [5–6, 24] and dip-coating methods [25]. This inconsistency between band gap and film thickness may come from the different level of crystallinity of the  $\text{TiO}_2$ . The degradation levels of MB agree well with the band gap of  $\text{TiO}_2$  films, in that the lower-band-gap 90-min films showed more MB degradation. Our result implies that the crystallinity of  $\text{TiO}_2$  films should be considered for photocatalytic efficiency in water purification.

### CONCLUSION

$\text{TiO}_2$  films were successfully synthesized on glass slides by chemical vapor deposition at the temperature of  $530^\circ\text{C}$ . The  $\text{TiO}_2$  film synthesized for 90 min showed greater degradation of methylene blue than the one prepared for 60 min even with a smaller band gap. The measured band gaps of the films prepared for 60 and 90 min were 3.51 and 3.25 eV, respectively. The crystallinity of the films synthesized for 90 min is much better than that for 60 min. We propose that the



crystallinity of TiO<sub>2</sub> films is an important factor to consider in the photodegradation of methylene blue, not only their band gap.

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