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## Photocatalytic TiO<sub>2</sub> deposition by chemical vapor deposition

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### Abstract

Dip-coating, spray-coating or spin-coating methods for crystalline thin film deposition require post-annealing process at high temperature. Since chemical vapor deposition (CVD) process is capable of depositing high-quality thin films without post-annealing process for crystallization, CVD method was employed for the deposition of TiO<sub>2</sub> films on window glass substrates. Post-annealing at high temperature required for other deposition methods causes sodium ion diffusion into TiO<sub>2</sub> film from window glass, resulting in the degradation of photocatalytic efficiency. Anatase-structured TiO<sub>2</sub> thin films were deposited on window glass by CVD, and the photocatalytic dissociation rates of benzene with CVD-grown TiO<sub>2</sub> under UV exposure were characterized. As the TiO<sub>2</sub> film deposition temperature was increased, the (112)-preferred orientations were observed in the film. The (112)-preferred orientation of TiO<sub>2</sub> thin film resulted in a columnar structure with a larger surface area for benzene dissociation. Obviously, benzene dissociation rate was maximum when the degree of the (112) preferential orientation was maximum. It is clear that the thin film TiO<sub>2</sub> should be controlled to exhibit the preferred orientation for the optimum photocatalytic reaction rate. CVD method is an alternative for the deposition of photocatalytic TiO<sub>2</sub>. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* TiO<sub>2</sub>; Photocatalytic; CVD; Preferred orientation

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## 1. Introduction

The development of novel, effective technologies for purifying air and water is an important social goal. Photocatalysts are materials, typically wide band gap semiconductors, activated by exposure to light whose energy exceeds the band gap energy of the material. When the material is activated, electron hole pairs are formed and the lifetime of these two types of carriers is different. Two types of carriers take part in the oxidation and reduction reaction. Photocatalysts have been studied over the years for a variety of applications: photochemical solar energy conversion, synthetic fuel production and the decomposition of hazardous substances [1–3].

Titanium dioxide activated by near ultraviolet (UV) light is by far the most widely studied photocatalytic material. Photocatalytic  $\text{TiO}_2$  has been an interesting subject for its water and air purification capabilities [4–8]. Recently, its application to self-cleaning capability became one of the interesting topics for the use of street or tunnel lighting [9]. This brings out the necessity of coating  $\text{TiO}_2$  on glass.

Physical vapor deposition (PVD) techniques like sputtering [10–14] and electron beam evaporation [15] have long been employed for the deposition of thin films of  $\text{TiO}_2$  for optical applications. Chemical vapor deposition (CVD) of  $\text{TiO}_2$  film was also used for dynamic random access memory applications [16]. These studies were all for dense, smooth, high index reflective coatings or high dielectric constants with rutile structures.

Dip-coating, spray-coating or spin-coating method has been the most commonly employed method for the deposition of anatase-structured photocatalytic  $\text{TiO}_2$  thin films. These methods require the post-annealing process for the crystallization into anatase structure. Furthermore, post-annealing process required for these deposition methods causes the sodium ion diffusion from window glass into  $\text{TiO}_2$  film and results in the degradation of photocatalytic efficiency. Sodium ion diffusion effect in  $\text{TiO}_2$  is dominant when the temperature is over  $450^\circ\text{C}$  and typical post-annealing temperature is above  $600^\circ\text{C}$ . Recently, use of  $\text{SiO}_2$  diffusion barrier was presented to prevent the sodium ion diffusion during post-annealing process [17]. However, CVD method does not require a post-annealing process and  $\text{SiO}_2$  diffusion barrier by depositing at relatively low temperature. Since CVD process is capable of depositing high-quality crystalline thin films, there is a great possibility to employ the CVD method for the deposition of  $\text{TiO}_2$  films on glass.

CVD method has another merit that the film structure can be easily controlled by deposition conditions. By suitable choice of deposition conditions, it is possible to produce films with a porous columnar structure resulting in larger area for photocatalytic reactions.

## 2. Experiment

Photocatalytic  $\text{TiO}_2$  thin film depositions were carried out in a vertical low-pressure CVD reactor. CVD reactor was home-built cold-wall type. Sources for titanium and oxygen were TTIP (tetrakispropoxide) and  $\text{O}_2$  gas, respectively. Deposition temperature was varied from  $287^\circ\text{C}$  to  $362^\circ\text{C}$ , and the processing pressure was kept at 1 Torr. Argon

gas was used as carrier gas for TTIP. Flow rate for argon and oxygen were 80 and 10 cm<sup>3</sup>/min, respectively. TTIP supply was  $4.464 \times 10^{-5}$  mol/min.

Microstructures of TiO<sub>2</sub> films were characterized by X-ray diffractometer (XRD) using Cu K<sub>α</sub> radiation at 40 kV and 20 mA. Surface morphologies and cross-sections of films were observed using scanning electron microscope (SEM).

Benzene degradation rates of 10 × 10 cm<sup>2</sup> size TiO<sub>2</sub> films on glass were carried out using gas chromatography (HP6890 series) in a quartz reactor with volume of 610 ml under UV light exposure (Sankyo BLB, λ = 365 nm) with 0.71 mW/cm<sup>2</sup> intensity at room temperature. Initial benzene concentration for the measurement was approximately

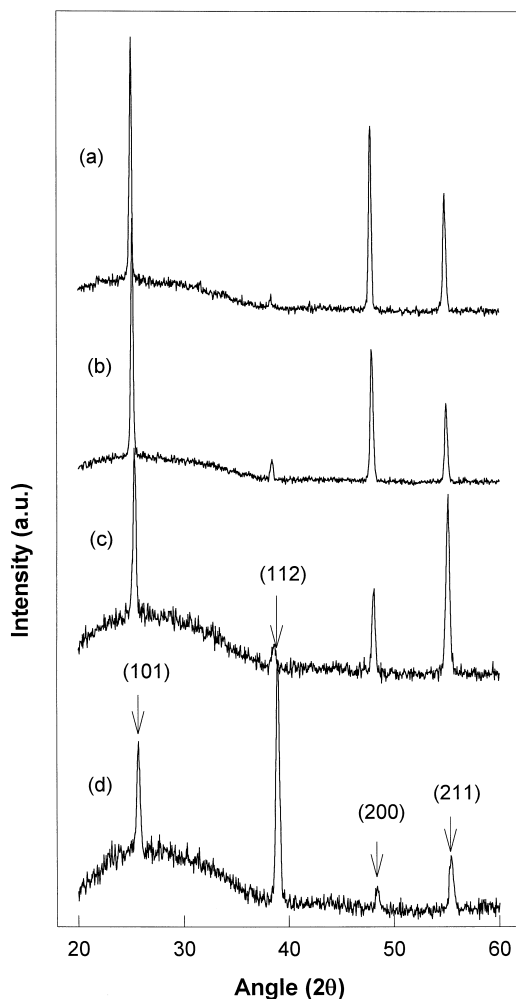


Fig. 1. The XRD spectra of TiO<sub>2</sub> films on glass deposited at various temperatures: (a) 287°C, (b) 306°C, (c) 325°C and (d) 362°C were presented. All specimens exhibited anatase structures and no rutile phase was detected.

120 ppm in reactor and under constant flow mode of GC with pressure, flow and average velocity are 18.5 psi, 0.9 ml/min (He) and 29 cm/s, respectively.

### 3. Results and discussion

The XRD spectra of  $\text{TiO}_2$  films on glass deposited at various temperatures were shown in Fig. 1. Typical film thickness was about  $1.3 \mu\text{m}$ . The films required no post-annealing in  $\text{O}_2$  environment to achieve the  $\text{TiO}_2$  stoichiometry. All specimens had the anatase structure and rutile phase was not found. Integrated intensity ratios,

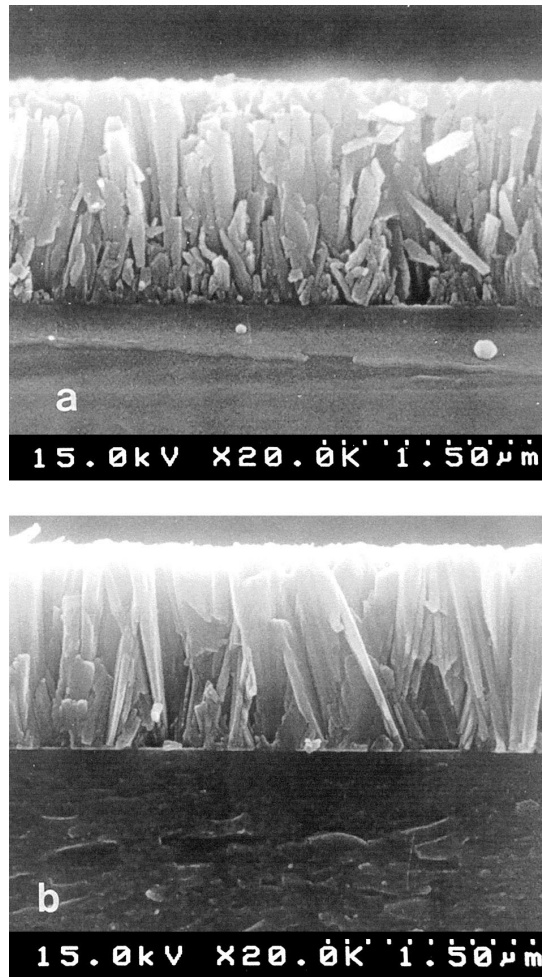


Fig. 2. Cross-sectional SEM micrographs of the specimens deposited at (a)  $325^\circ\text{C}$  and (b)  $362^\circ\text{C}$  were presented. Both specimens showed the well-developed columnar structure.

$I_{(101)}/I_{(112)}$ , were varied with  $\text{TiO}_2$  deposition temperatures. Comparing with the anatase-structured powder XRD spectrum [18], the films deposited at lower temperature at 287°C and 306°C showed no preferred orientation and exhibited the random directional growth with high integrated intensity ratios,  $I_{(101)}/I_{(112)}$ , as seen in Fig. 1. However, the films deposited at higher temperature at 325°C and 362°C exhibited the lower integrated intensity ratio of  $I_{(101)}/I_{(112)}$  as seen in Fig. 1. It could be clearly seen that the sample grown at 362°C exhibited the highest degree of preferred orientation of (112) among these specimens. This clearly indicated that the preferred orientation was gradually developed to (112) with increasing deposition temperature. Reactants at sufficiently high temperature would have enough energy to find the sites for preferential growing.

Cross-sectional view of the specimens grown at 325°C and 362°C is presented in Fig. 2. Films deposited at lower temperatures exhibited the random direction of growth. As the deposition temperature increases, columnar structures were developed. The films deposited above 325°C showed the well-developed columnar structures as seen in Fig. 2. The film deposited at 325°C exhibited the higher integrated intensity ratio,  $I_{(101)}/I_{(112)}$ ,

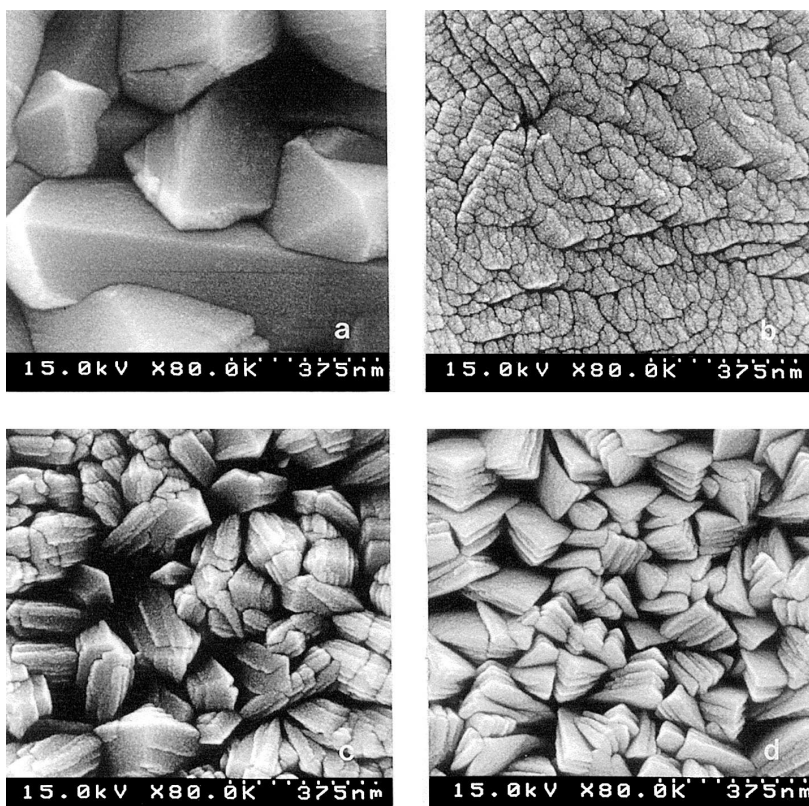


Fig. 3. Surface SEM micrographs of the specimens shown in Fig. 1 are presented. Samples were deposited at: (a) 287°C, (b) 306°C, (c) 325°C and (d) 362°C.

than the specimen grown at 362°C as seen in Fig. 1. Figs. 1 and 2 were consistent, since the growth direction of columns in 325°C-grown specimens was shown to be relatively tilted than that of 362°C-grown one. Film deposited at 362°C showed well-developed columnar structure with smaller column diameter, and the columns were grown in vertical direction from interfaces between the film and substrate and aligned parallel to each other which resulted in the higher degree of the (112)-preferred orientation deposition of TiO<sub>2</sub>.

Surface morphologies of the specimens grown at various temperatures were observed by SEM as seen in Fig. 3. Surface morphologies were changed gradually with the development of preferred orientation with increasing deposition temperature. The void areas on the surface increased with increasing deposition temperature. This result implied that more voids were formed with the increasing degree of the (112)-preferred orientation, comparing with Fig. 1.

To see the benzene degradation rates of TiO<sub>2</sub> on glass deposited at various temperatures with UV exposure, benzene concentration variations as a function of reaction time in the reactor are monitored and shown in Fig. 4. TiO<sub>2</sub> films all had anatase structure with similar film thickness as seen in Fig. 1. When the deposition temperature was below 306°C, effect of TiO<sub>2</sub> with random growth directions on benzene degradation was not noticeable. TiO<sub>2</sub> films grown above 325°C exhibited benzene degradation characteristics with UV exposure as seen in Fig. 4. Films grown above 325°C had columnar

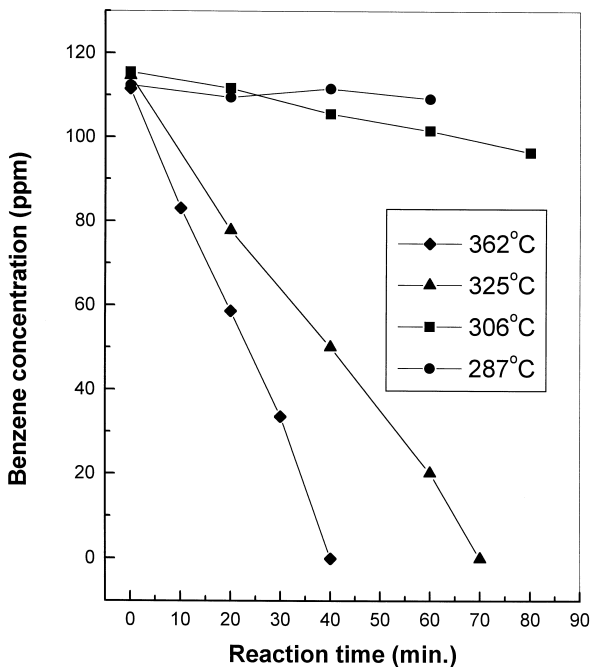


Fig. 4. Benzene degradation effect of 10 × 10 cm<sup>2</sup> size TiO<sub>2</sub> films in Fig. 1 under UV exposure was monitored and presented. Film deposition temperatures are marked in the insert.

structure with voids as seen in Figs. 2 and 3. Best benzene degradation rate was observed for the TiO<sub>2</sub> deposited at 362°C, resulting from higher degree of (112)-preferred orientation.

Grains in the film with random directional growth would meet each other, and there is higher possibility to close the voids as seen in Fig. 3. However, the columnar grains with high degree of preferred orientation would have less chance to meet other grains and form the deep voids even though the voids are not connecting the film surface and the interface between film and substrate. It is not clear how deep the voids formed on the film surfaces are; however, it is clear that the columnar structure with preferred orientation exhibits higher photocatalytic efficiency since the columns with preferred orientation have higher probability to form deeper voids. This result agrees well with Weinberger and Garber [19] who said that the columnar structured TiO<sub>2</sub> films with preferred orientation exhibited more surface area for photocatalytic reaction since columns with preferred orientation, which consist of columns, were separated by small voids.

#### 4. Conclusion

TiO<sub>2</sub> films deposited on glass by CVD exhibited the higher degree of (112)-preferred orientation with increasing deposition temperature. Compare to TiO<sub>2</sub> powder, the TiO<sub>2</sub> in forms of thin film possessed relatively smaller surface area for photocatalytic reaction. Integrated intensity ratio,  $I_{(101)}/I_{(112)}$ , showed the minimum value for TiO<sub>2</sub> deposited at 362°C where the degree of preferred orientation to (112) was highest. The (112)-preferred orientation of films resulted in the larger surface area for photocatalytic reaction by forming columnar structure with deeper voids on the film surface. With UV exposure, the benzene dissociation rate of TiO<sub>2</sub> film deposited at 362°C was the best among the specimens. This implies that for the best photocatalytic reaction rate, it is suggested that the TiO<sub>2</sub> film should be deposited to have the preferred orientation with columnar structure for the formation of larger surface area for dissociative reaction. It is also clear that the CVD process is an alternative for photocatalytic TiO<sub>2</sub> deposition.

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