Materials Science and Engineering B 113 (2004) 42–45

www.elsevier.com/locate/mseb

Photocatalytic TiO_2 thin films prepared via a high-pressure crystallization process

Chung-Hsin Lu*, Wei-Hong Wu

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, ROC

Received 31 May 2004; accepted 23 June 2004

Abstract

Titania thin films with high photocatalytic activity are successfully synthesized by combining the metalorganic deposition method (MOD) and the high-pressure crystallization (HPC) process. The crystallization temperature of anatase-type TiO_2 films is significantly reduced to as low as 150 °C. TiO_2 thin films with crack-free surface and uniform morphology are obtained. The diffusion of silicon species from substrates into TiO_2 films is effectively suppressed. The HPC-derived TiO_2 thin films are demonstrated to have higher photocatalytic activity than those prepared via the conventional annealing process.

Keywords: Photocatalytic; Titanium dioxide; Anatase; Thin films

1. Introduction

In recent years, titanium dioxide (TiO_2) has been extensively applied in various fields such as dielectric materials, gas sensors, dye-sensitized solar cells, pigments, and photocatalysts [1–5]. Ever since Fujishima [6] discovered that TiO_2 can split water under UV light illumination, the photocatalytic activity of TiO_2 has attracted great attention and has been widely investigated [7,8]. There are various methods to synthesize TiO_2 thin films, such as the sol–gel method, the sputtering method, and the chemical vapor deposition (CVD) method. The most commonly adopted method for preparing photocatalytic TiO_2 thin films is the sol–gel method because of the advantages of simplified processes and low cost of materials. M. J. Alam et al. deposited TiO_2 thin films on silicon and glass substrates via the sol–gel process using titanium iso-propoxide [9], and reported that the crystallized TiO_2 with an anatase structure is obtained after annealing at above 400 °C. Yu et al. [10] stated that the diffusion of sodium and calcium ions from the soda-lime glass into the TiO_2 films is detrimental to the photocatalytic activity of the obtained TiO_2 films. Since high-temperature heating will facilitate the interdiffusion of TiO_2 and other substances in the substrates, the photocatalytic activity of TiO_2 will be diminished.

In order to lower the crystallization temperature of ceramic thin films, a high-pressure crystallization (HPC) process was recently developed by our group to prepare crystallized ceramic thin films at low temperatures [11–13]. Dielectric Ta_2O_5 and ferroelectric $Pb(Zr,Ti)O_3$ (PZT) thin films are both successfully crystallized via the HPC process at a temperature as low as 350 °C, which is significantly lower than the crystallization temperatures in the conventional annealing process under atmospheric pressure. In this study, the HPC process is employed to lower the crystallization temperature of TiO_2 thin films. The phase formation and photocatalytic activity of the films obtained via the HPC process are investigated.

2. Experimental

The precursor films of titanium dioxide were prepared via the metalorganic deposition method (MOD). Titanium tetraisopropoxide and 2-methoxylethanol were used as the

* Corresponding author. Tel.: +886 2 23651428; fax: +886 2 23623040.
E-mail address: chlu@ccms.ntu.edu.tw (C.-H. Lu).

0921-5107/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2004.06.013

source metalorganic solution and solvent, respectively. N-type silicon wafers were utilized as the substrates. The metalorganic solution was spin-coated onto the cleaned silicon substrates. The coated substrates were dried on the hot plate at 150 °C for 10 min to remove the organic solvent. The dried thin films on substrates were further pyrolyzed at 325 °C for 30 min to evaporate the residual organics. The above process was repeated for three times to obtain the desired film thickness (around 0.4 μm).

The as-pyrolyzed films were annealed via two different crystallization processes. The first one was annealing in a furnace under atmospheric pressure (14.7 psi) at various temperatures ranging from 325 to 600 °C for 2 h, and the other one was to anneal via the HPC process at 125–250 °C for 2 h. During the HPC process, the as-pyrolyzed films were annealed in a sealed stainless-steel bomb containing distilled water to form a high-pressure environment. The as-pyrolyzed films were placed above the water surface to avoid contact with water. In order to verify the crystal structure of TiO_2 thin films, X-ray source with stronger intensity and a specific wavelength of 1.32679 Å was dispersed from continuous synchrotron radiation, and the phases existent in the films were analyzed. The surface morphologies of the thin films were examined via a scanning electron microscope (SEM). The depth profiles of the annealed films were analyzed via secondary ion mass spectroscopy (SIMS). The photocatalytic activity of the TiO_2 thin films was determined based on the degradation of methylene blue. UV–vis spectroscopy was utilized to detect the absorbance of the degraded methylene blue. The illuminance of UV light source used during the photocatalysis process was about 1.2 mW/cm^2.

3. Results and discussion

Fig. 1(a) illustrates the X-ray diffraction (XRD) patterns of the as-pyrolyzed films annealed under atmospheric pressure (14.7 psi). In this figure, the films annealed at 325°C show no diffraction peaks, indicating that the films remain at their amorphous state. After annealing at 350 °C, crystalline TiO_2 with an anatase structure is formed. When annealing temperature reaches 600 °C, the crystallinity of TiO_2 thin film is enhanced. The XRD patterns of the as-pyrolyzed films annealed via the HPC process are illustrated in Fig. 1(b). After 125 °C annealing under 30 psi via the HPC process, only amorphous films are obtained. However, once the as-pyrolyzed films are annealed at 150 °C under 70 psi, the amorphous films are converted to crystallized TiO_2 films. In comparison with the conventional annealing process under atmospheric pressure, the HPC process significantly reduces the crystallization temperature from 350 to 150 °C. When the as-pyrolyzed films are further annealed at 250 °C under 588 psi, the crystallinity of TiO_2 is greatly improved. The HPC process might lead to a reduction in the critical free energy required for the formation of stable nuclei, and facilitates the nucleation process at low temperatures [14,15]. The other possible mechanism

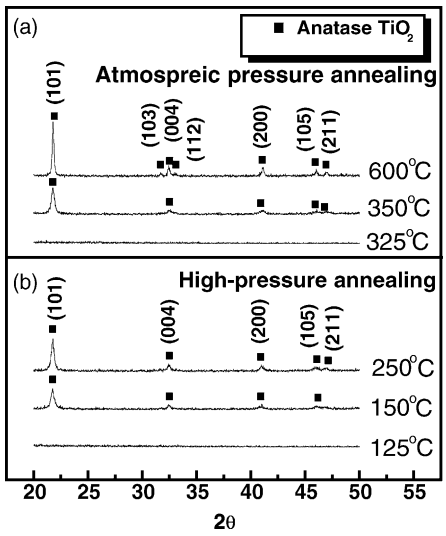

Fig. 1. X-ray diffraction patterns of TiO_2 thin films annealed under: (a) atmospheric pressure; and (b) high pressure.

is that the high vapor-pressure developed during the process probably forms a water coating on the film surface, thereby resulting in a dissolution–precipitation process to produce the crystallized nuclei at low temperatures.

The surface morphologies of TiO_2 thin films were analyzed by SEM, and the obtained scanning electron micrographs are shown in Fig. 2. As demonstrated in Fig. 2(a), after 150 °C annealing under 30 psi in the HPC process, uniform TiO_2 thin films without cracks are formed, and the particle size of the obtained thin films is around 30 nm. After TiO_2 thin films are annealed at 250 °C under 588 psi in the HPC process, the particle size of the thin films slightly enlarges to 50 nm as shown in Fig. 2(b). Contrarily, it is shown in Fig. 2(c) that with 600 °C annealing under atmospheric pressure, cracks are formed randomly on the film surface and the microstructure of the thin films appears porous. The cracking is considered to be owning to the stress caused by uneven thermal expansion, and the interfacial roughening as well as voids formed during high-temperature annealing [16]. The above results indicate that the formation of undesired cracks on the surface of TiO_2 thin films is effectively avoided via the HPC process.

Fig. 3 illustrates the depth profiles of TiO_2 thin films annealed at 600 °C under atmospheric pressure (14.7 psi) and at 250 °C under 588 psi. After 600 °C annealing under atmospheric pressure, silicon species diffuse from substrates into TiO_2 films, and the diffusion distance of Si species is 0.15 μm as depicted in Fig. 3(a). On the other hand, after 250 °C annealing under 588 psi in the HPC process, the diffusion distance of Si species from substrates into TiO_2 thin films is merely 0.08 μm (Fig. 3(b)). Since the annealing temperature in the HPC process is much lower than that of the conventional method, the diffusion rate and mobility of Si species are considerably reduced in the HPC process. It is demonstrated that the interdiffusion between TiO_2 thin

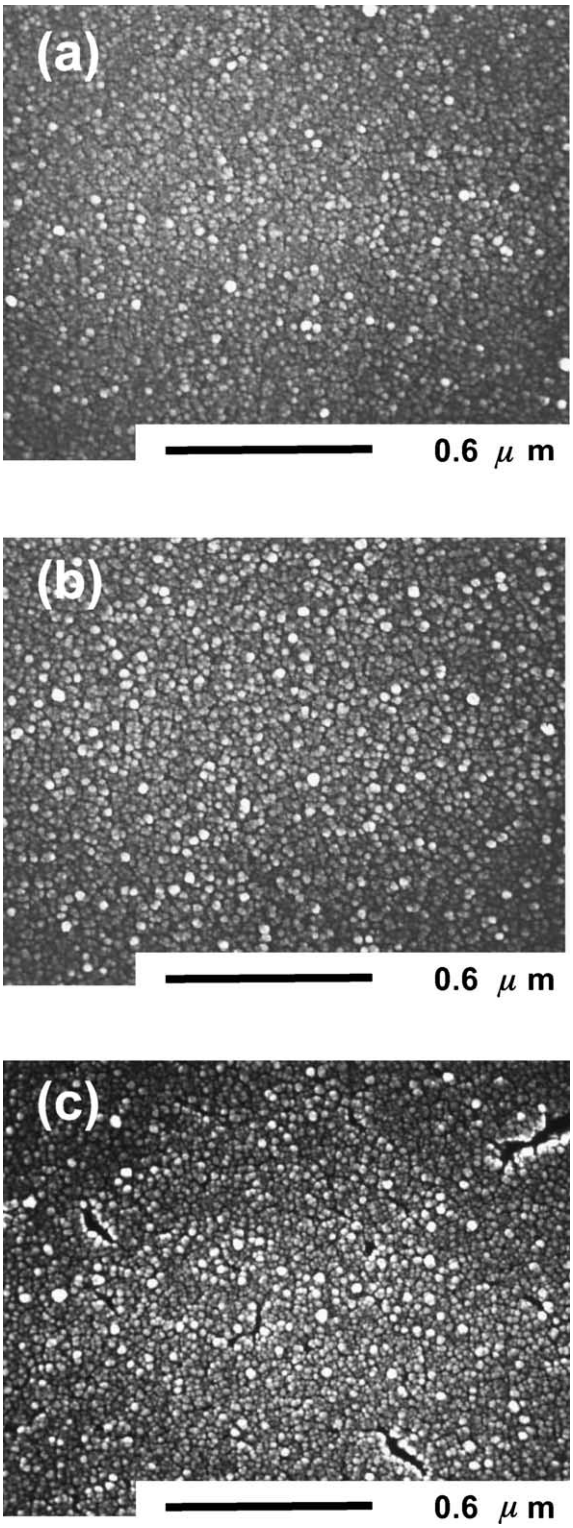

Fig. 2. Scanning electron micrographs of TiO_2 thin films prepared at: (a) 150 °C under 63 psi (HPC process); (b) 250 °C under 588 psi (HPC process); and (c) 600 °C under 14.7 psi (atmospheric pressure annealing).

films and substrates is effectively suppressed by the HPC process.

The absorbance changes of methylene blue solution degraded by the TiO_2 thin films are illustrated in Fig. 4. It

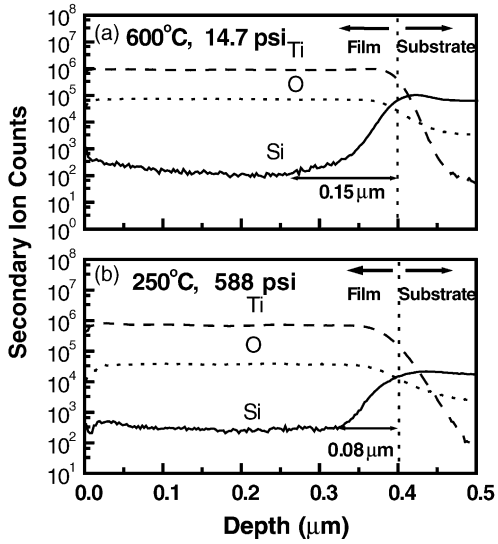

Fig. 3. Secondary ion mass spectroscopic profiles of TiO_2 thin films annealed at: (a) 600 °C under 14.7 psi (atmospheric pressure annealing); and (b) 250 °C under 588 psi (HPC process).

is found that the photocatalytic activity of the amorphous films is low since the absorbance of methylene blue solution changes very little (curve a). When TiO_2 thin films are annealed at 350 °C under atmospheric pressure, the photocatalytic activity is improved; however methylene blue is only partially degraded (curve b). The thin films annealed at 150 °C via the HPC process have greater photocatalytic activity than those annealed at 350 °C under atmospheric pressure (curve c). Methylene blue is completely decomposed after 5 h-illumination for the films annealed at 600 °C under atmospheric pressure and those annealed at 250 °C under 588 psi (curves d and e). However, the degradation rate of TiO_2 thin films annealed at 250 °C via the HPC process is faster than

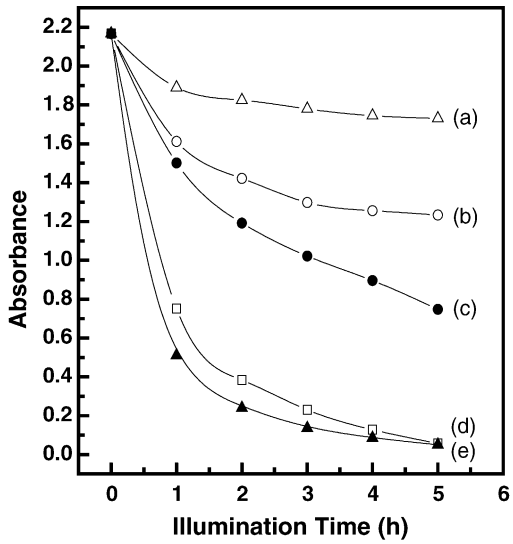

Fig. 4. Degradation of methylene blue for (a) amorphous TiO_2 films and TiO_2 thin films annealed at: (b) 350 °C under 14.7 psi; (c) 150 °C under 63 psi; (d) 600 °C under 14.7 psi; and (e) 250 °C under 588 psi.

that of films annealed at 600 °C under atmospheric pressure. It is revealed that TiO_2 thin films prepared via the HPC process have greater photocatalytic activity than those derived from the conventional annealing process. It is reported that the diffusion of substrate species is detrimental to the photocatalytic activity of TiO_2 thin films [17,18]. Substrate species will not only decrease the photocatalytic activity of TiO_2, but also produce surface and bulk recombination centers of photogenerated electron–hole pairs. The diffusion of Si species into TiO_2 films will reduce the photocatalytic activity of TiO_2 films when they are annealed at high temperatures. For TiO_2 films, it is confirmed that the HPC process can effectively reduce their crystallization temperature and significantly improve their photocatalytic activity.

4. Conclusions

Titania thin films with a monophasic anatase structure are synthesized in this study. The crystallization temperature of TiO_2 films is significantly reduced to as low as 150 °C via the newly developed HPC process. TiO_2 thin films with crack-free surface are successfully obtained via this process. The diffusion of silicon species from substrates is effectively suppressed because of the lowered annealing temperatures. It is demonstrated in this study that TiO_2 films prepared via the HPC process exhibit enhanced photocatalytic activity in comparison with those derived from the conventional annealing process. The developed process provides a novel route to synthesize TiO_2 thin films with high photocatalytic activity at low temperatures.

Acknowledgement

The financial support for this study from Ministry of Economic Affair, Taiwan, the Republic of China through Grant 92-EC-17-A-09-S1-019 is gratefully acknowledged.

References

[1] G.K. Dalapati, S. Chattejee, S.K. Samanta, C.K. Maiti, Electron. Lett. 39 (2003) 323.
[2] A. Ruiz, A. Cornet, G. Sakai, K. Shimanoe, J.R. Morante, N. Yamazoe, Chem. Lett. 9 (2002) 892.
[3] K. Hara, Y. Tachibana, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, Sol. Energy Mater. Sol. C 77 (2003) 89.
[4] P. Gross, J. Schmelzer, Macromol. Symp. 187 (2002) 641.
[5] L. Zhang, Y.F. Zhu, Y. He, W. Li, H.B. Sun, Appl. Catal. B Environ. 40 (2003) 287.
[6] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[7] D. Robert, B. Dongui, J.V. Weber, J. Photochem. Photobiol. A 156 (2003) 195.
[8] P.A. Christensen, T.P. Curtis, T.A. Egerton, S.A.M. Kosa, J.R. Tinlin, Appl. Catal. B Environ. 41 (2003) 371.
[9] M.J. Alam, D.C. Cameron, J. Sol–Gel Sci. Technol. 25 (2002) 137.
[10] J. Yu, X. Zhao, Mater. Res. Bull. 35 (2000) 1293.
[11] C.H. Lu, US Patent No. 6,143,366 (2000).
[12] C.H. Lu, Y.C. Chen, Y.C. Sun, J. Mater. Chem. 12 (2002) 1628.
[13] C.H. Lu, W.J. Hwang, Y.C. Sun, Jpn. J. Appl. Phys. 41 (2002) 6674.
[14] S.C. Liao, W.E. Mayo, K.D. Pae, Acta Mater. 45 (1997) 4027.
[15] K.W. Seo, J.K. Oh, J. Ceram. Soc. Jpn. 108 (2000) 691.
[16] J. Lee, S.H. Oh, J. Lee, E. Lee, I. Lim, W.K. Park, G. Kim, Thin Solid Films 370 (2000) 307.
[17] Y. Paz, A. Heller, J. Mater. Res. 12 (1997) 2759.
[18] Y. Paz, Z. Luo, L. Rabenberg, A. Heller, J. Mater. Res. 10 (1995) 2842.