

Crystallinity and photocatalytic activity of liquid phase deposited TiO₂ films

B. Ma · G. K. L. Goh · J. Ma

© Springer Science + Business Media, LLC 2006

Abstract Anatase TiO₂ films were deposited on glass substrates at 50 and 200°C to investigate the effect of growth temperature on the photocatalytic activity of the films. It was observed that the films grown at 200°C were composed of columnar crystallites and were more porous than the films grown at 50°C which had more compact structures. Also, the film crystallinity increased from 75 to 90% if the higher growth temperature was used. Despite the higher crystallinity, it was observed that for crystallinities between 60 and 90%, the photocatalytic behavior of the films was more significantly affected by changes in the surface area.

Keywords TiO₂ · Photocatalysis · Crystallinity

1 Introduction

Titanium dioxide is one of the most studied photocatalyst due to its low cost, excellent optical transmittance and good chemical stability. The anatase phase is generally the more photocatalytically active phase compared with rutile and brookite [1], and its photocatalytic ability has been used especially in the photodegradation of organic pollutants for self-cleaning and solvent purification applications and also as antibacterial coatings [2, 3]. Since thin films or coatings are required for practical applications, techniques for depositing

anatase thin films with high activity have attracted a great deal of attention.

Liquid phase deposition (LPD) has been used extensively to grow amorphous or partially crystalline TiO₂ on a variety of substrates at temperatures of 60°C and lower [4–9]. The low deposition temperature allows the use of temperature sensitive substrates like polymers. This allows for greater flexibility in material combinations that could lead to devices with greater and more varied functionality. Another important advantage is that irregular and porous bodies can be coated evenly as deposition is not a line-of-sight process.

Generally, high surface areas and high crystallinity are important for achieving good photocatalytic activity [10]. As such, researchers commonly subject the films to post deposition heat treatments of 200°C and higher to induce or increase crystallinity. However, these heat treatments invariably decrease the surface area and limit the choice of substrates. In this report, anatase films were deposited at 50 and 200°C by LPD to determine if the higher crystallinity attained by the 200°C process produces greater photocatalytic activity without the need for post deposition heat treatments.

2 Experimental

TiO₂ films were grown on glass substrates suspended horizontally by a PTFE holder and placed in glass beakers for depositions at 50°C or Teflon-lined acid digestion bombs (Parr) for depositions at 200°C. The glass substrates were previously cleaned with 4 parts H₂SO₄ and 1 part H₂O₂ for 15 min followed by a deionised water rinse prior to use. Aqueous solutions of ammonium hexafluorotitanate, (NH₄)₂TiF₆, and boric acid, B₂O₃, were mixed and stirred to form a precursor solution containing 0.1 M (NH₄)₂TiF₆ and 0.2M boric acid. Films were then grown at 50°C and 200°C for periods

B. Ma · G. K. L. Goh (✉)
Institute of Materials Research and Engineering, 3 Research Link,
Singapore 117602, Singapore
e-mail: g-goh@imre.a-star.edu.sg

B. Ma · J. Ma
School of Materials Science and Engineering, Nanyang
Technological University, Singapore 639798, Singapore

ranging from 15 min to 24 h. (Note that the solutions in the reactors were observed to take approximately 90 min to reach the set temperatures of 50, 80 and 100°C and is assumed to be the same for the set temperature of 200°C). After cooling to room temperature, the films were washed with distilled water and dried at room temperature. The powder precipitated simultaneously with film formation was washed by successive centrifugation and then dried at 50°C for 24 h. The Brunauer-Emmett-Teller (BET) surface area of the powder was determined by nitrogen physisorption (Micrometrics ASAP 2010).

The crystallinity of the precipitated powders were determined by first mixing each sample with 20 wt% of a standard alumina powder of 100% crystallinity. Powder X-ray diffraction (XRD) patterns were then recorded from $2\theta = 10$ to 80° in increments of 0.02° and a scan rate of $0.045^\circ/\text{min}$ with a Rigaku Dmax 2200 employing $\text{Cu K}\alpha$ radiation. Structure refinements were then performed by a Rietveld method using a fundamental parameters procedure [11]. By comparing the weight percentage of the alumina, X , determined from the Rietveld refinement with the known weight percentage in the mixture (20 wt%), the weight percentage of amorphous material, W_o , in the mixture can be determined according to,

$$W_o = 1 - 20\%/X \quad (1)$$

From Eq. (1), the percentage crystallinity of the TiO_2 material, W , is determined as,

$$W = 1 - 80\%/W_o \quad (2)$$

The photocatalytic activities of the films were evaluated by the degradation of methyl orange. Four pieces of film with a total surface area of 9.68 cm^2 were placed in a glass container containing a $15 \text{ ml } 1 \times 10^{-5} \text{ M}$ methyl orange solution. This set up was placed in a UV reaction chamber (RPR-100) where the light intensity at 365 nm at the center of the glass container was $213 \mu\text{W}/\text{cm}^2$. The concentration of methyl orange remaining after each experiment was determined with a UV-VIS-NIR scanning spectrophotometer (Shimadzu UV-3101PC).

3 Results and discussions

3.1 Structure

To understand how the different deposition temperatures affected the film structure, the cross sections of films grown at 50 and 200°C were examined, as shown in Fig. 1. For both films, the film can be separated into two regions. The region closer to the film/substrate interface is composed of densely packed crystallites, probably because nucleation was more

dominant then growth at the earlier stages of film deposition. The region closer to the film surface is composed of more columnar like crystallites as growth became more dominant as the reaction progressed and the supersaturation decreased. In addition, the growth region is larger for higher deposition temperatures as growth is more dominant at higher temperatures. The structure of the powders precipitated simultaneously with film deposition also display similar structures, as shown by fractured particles in Figs. 1(b) and (d).

Films with columnar structures tend to be porous as pores can be formed at the junctions of neighboring crystallites [12]. Therefore, the 200°C film could likely be more porous than the 50°C film. When growth is dominant, the columnar crystallites not only grow upwards, they also grow larger laterally by consuming surrounding crystallites. This is expected to reduce the porosity of the film. Since the pores are the source of internal surface area (as compared to the external area of the film surface), this translates to the reduction of internal surface area as film deposition progresses. Also, as columnar crystallites form the majority of the film for the 200°C film as compared to the 50°C film, this reduction in surface area with deposition time is expected to affect the 200°C film more significantly.

To get an idea if the proposed reduction actually occurred, the specific surface area of the powders precipitated in the same solution in which the films were grown were determined by nitrogen physisorption. The results are shown in Table 1, which also shows the film thickness for the corresponding deposition time and temperature. As proposed earlier, the specific surface area for the TiO_2 material precipitated at 200°C decreased as deposition time progressed. On the other hand, the specific surface areas for the 50°C TiO_2 material stayed relatively constant with deposition time, but were all lower than that of the 200°C material.

3.2 Crystallinity

To investigate the effect of the deposition temperature, the crystallinity of the TiO_2 material precipitated were determined by X-ray diffraction (XRD) and Rietveld structure refinements. The crystallinities of the precipitated TiO_2 material at the set temperatures of 50 and 200°C for the different deposition times are shown in Fig. 2. This figure shows that the maximum crystallinity for material grown at 200°C was 90% while the maximum was 75% at 50°C. The crystallinities at both set temperatures were also observed to increase with deposition time. This is because the temperature in the reactors took approximately 90 min to reach the set temperatures so that material precipitated at shorter periods would have done so at temperatures lower than the set temperature of 50 or 200°C. At 50°C, the crystallinity is still increasing even after 4 h because the lower crystallinity

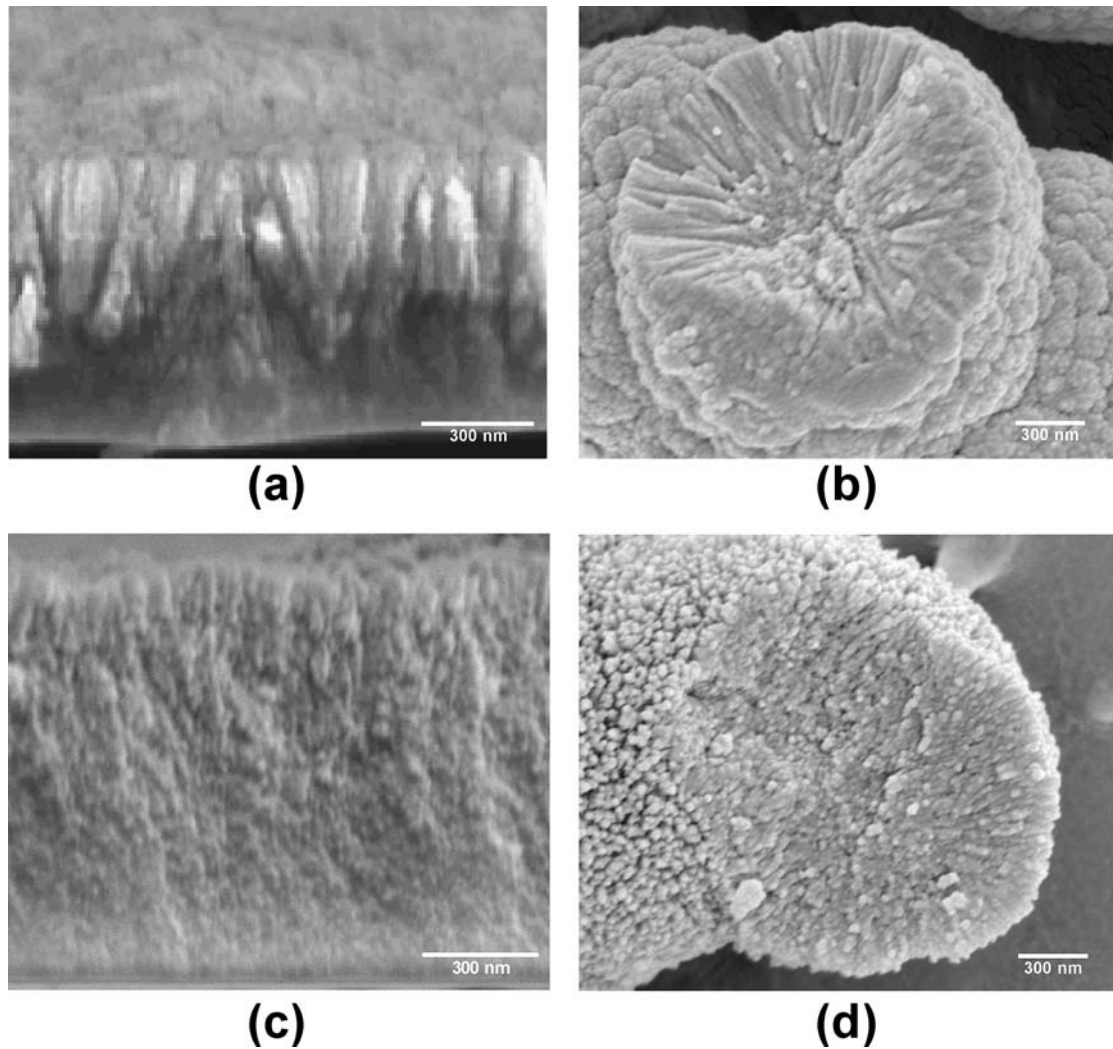


Fig. 1 SEM micrographs of cross sections of films grown at set temperatures of (a) 200°C after 40 min, and (c) 50°C after 12 h, and the corresponding powders for (b) 200°C and (d) 50°C

material precipitated before the set temperature of 50°C was attained is still present.

In the liquid phase deposition (LPD) process, the hexafluorotitanate ion first undergoes a hydrolysis reaction followed by a dehydration reaction, as shown in Eqs. (3) and (4)

respectively, before TiO₂ is finally formed.

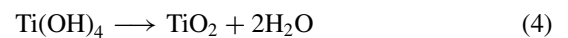
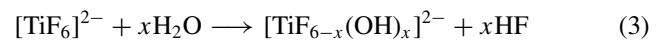


Table 1 Information regarding film thickness, crystallinity and specific surface area for growth at set temperatures of 50 and 200°C and various reactions periods

Set temperature	Reaction time	Film thickness (nm)	Crystallinity of powders (%)	Specific surface area of powders (m ² /g)	Degradation rate, $k \times 10^{-4}$ (min ⁻¹)
50°C	4 h	475	70	8.42	20
	6 h	591	72	10.1	17.9
	12 h	1020	75	9.8	29
200°C	20 min	455	64	90.83	32.4
	30 min	604	78	66.53	38.3
	40 min	1100	85	27.01	34.2

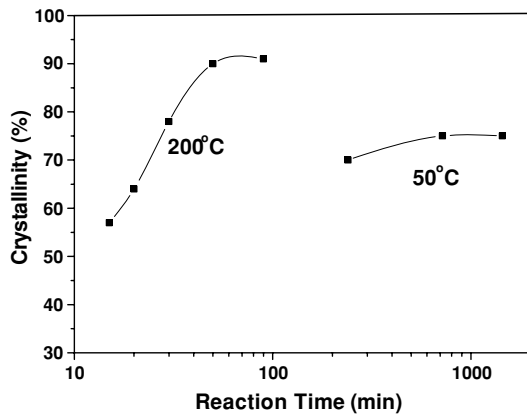
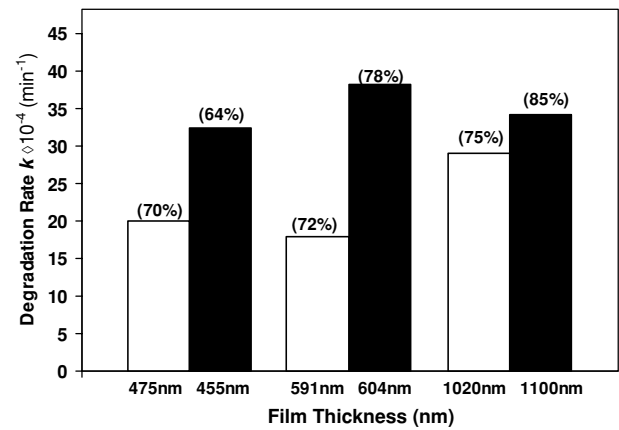


Fig. 2 Crystallinity of TiO₂ material precipitated at set temperatures of 50 and 200°C for different reaction periods.

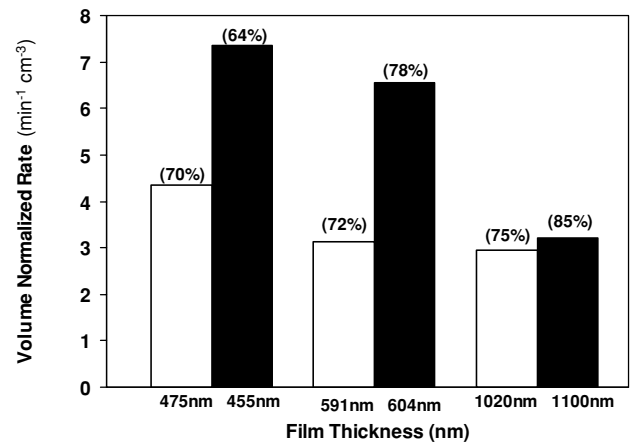
It is believed that higher growth temperatures accelerate the hydrolysis reaction, thereby promoting higher crystallinity [13]. But, Goh and co-workers [14] pointed out that even if the hydrolysis and dehydration reactions were complete, the TiO₂ material formed may not necessarily be crystalline. This is because crystalline anatase TiO₂ is formed when the octahedral titanium complexes repeatedly connect through shared edges in a periodic fashion to form skewed chains via dehydration reactions between the OH ligands of the octahedral complexes [15]. Goh and co-workers [14] proposed that protons (whether as hydroxyl groups or water molecules) not removed due to incomplete dehydration reactions disrupted the orderly formation and linking of chains, thereby leading to lowered degrees of crystallinity. Since the dehydration reactions would conceivably be less complete at lower growth temperatures, this would translate to lower crystallinities. It is added here that incomplete hydrolysis could also inhibit crystallization if the TiF₆²⁻ ions were incorporated in the final precipitated material as such ions would disrupt the long range periodicity required to form crystalline material.

3.3 Photocatalytic activity

The photodegradation of methyl orange by films grown at 50 and 200°C and of various thicknesses was observed to be a pseudo-first-order reaction and its kinetics may be expressed as $\ln(C_o/C) = kt$ where k is the photodegradation rate constant and C_o and C are the initial and final concentrations of methyl orange after time t . UV illumination of aqueous methyl orange solutions in the absence of TiO₂ films resulted in a degradation rate (blank constant) of $0.15 \times 10^{-4} \text{ min}^{-1}$. Photodegradation of methyl orange solutions with TiO₂ films present yielded rate constants two orders of magnitude higher, as shown in Fig. 3(a), and also in Table 1. Therefore it can be safely said that the photodegradation



(a)



(b)

Fig. 3 Photocatalytic activities of the films deposited at set temperatures of 50°C (white bars) and 200°C (black bars) as characterized by the (a) photodegradation rate, k , and (b) volume normalized degradation rate. (Percentages in brackets above each column denote the crystallinity of each film as determined from Fig. 2)

behaviors observed in Fig. 3 were due to the presence of TiO₂ films.

It is difficult to compare the photocatalytic behaviors of the films in Fig. 3(a) as the films have different thicknesses. In order to determine the effect of crystallinity on the photocatalytic activity of the films, the photodegradation rates are normalized by the volume of the respective films (since a larger volume of film would translate to a greater surface area), as shown in Fig. 3(b). The crystallinity of each film is also indicated in the brackets in Fig. 3 and as shown earlier in Fig. 2, the crystallinity increases with film thickness, that is, with longer deposition times. This is in contrast to the volume normalized degradation rate which decreases with increasing film thickness, more significantly for the 200°C material. Table 1 show that the specific surface areas also decrease with increasing film thickness. Therefore it appears that for crystallinities between 60 and 90%, it is the surface area that has a more dominant effect on the photocatalytic

activity and is responsible for the decrease in degradation rates.

To the authors' knowledge, there is only one other study where the photocatalytic activity of LPD TiO₂ films was tested by the photodegradation of methyl orange. This study was conducted by Yu and co-workers [13] who reported a maximum degradation rate, k , of $18.5 \times 10^{-4} \text{ min}^{-1}$. The TiO₂ film tested had been deposited on glass substrates (80 cm²) at room temperature and subjected to various annealing temperatures to induce crystallinity as the as-deposited film was amorphous. It was found that films annealed at 700°C, with a film thickness of 250 nm, displayed the highest degradation rate in methyl orange solutions under UV irradiation with an intensity of 112 μW/cm². In order to compare this rate with the results obtained in this study, the rate was normalized by the volume of film under UV irradiation, giving a volume normalized degradation rate of 0.925 min⁻¹ cm⁻³. This is still three times lower than the lowest rate of 2.94 min⁻¹ cm⁻³ obtained in this study for a film grown at 50°C for 12 h that is 1020 nm thick. The highest volume normalized degradation rate obtained in this work is 7.36 min⁻¹ cm⁻³ for a film grown at 200°C for 20 min that is 455 nm thick. Yu and co-workers did not measure the crystallinity of their material, but it is reasonable to assume that their films were of high crystallinity (at least more than the lowest crystallinity of 64% examined in this study) due to the annealing at 700°C. Therefore, it is most probable that the surface area of the films in this work are much higher and explains the higher degradation rates obtained.

Although there appears to be no study on the effect of UV intensity on the photodegradation of methyl orange by TiO₂, Chen and Ray [16] observed that the rate increased with the square root of intensity in the photodegradation of 4-nitrophenol by TiO₂. If this dependence on the UV intensity is assumed to be true for the photodegradation of methyl orange, then the adjusted volume normalized degradation rate works out to be 1.28 min⁻¹ cm⁻³, which is still more than 2 times lower than the minimum rate obtained in this study.

4 Conclusions

Anatase TiO₂ films of varying crystallinities and surface areas were deposited on glass substrates at 50 and 200°C by liquid phase deposition. The crystallinity increased with deposition time but saturated at 75 and 90% for the lower and higher growth temperatures respectively. It is believed that defects due to incomplete hydrolysis and dehydration

reactions inhibited and disrupted the periodic ordering that is required for crystallization.

Films and powders grown at 200°C had a more columnar structure as deposition progressed while the structure was more compact at 50°C. This was because growth was more dominant at the higher temperature while nucleation was more dominant at the lower growth temperature. A result of the columnar crystallites is that the 200°C films were more porous but the specific surface area also decreased more significantly with deposition time than the 50°C films due to crystal growth.

It was observed that crystallinity did not have a significant effect on the photodegradation of methyl orange for crystallinities above 60%. Instead, it is the surface area that has a more significant effect. The highest photodegradation rate of $38.8 \times 10^{-4} \text{ min}^{-1}$ was achieved by a 604 nm thick film deposited at 200°C for 30 min.

Acknowledgments The authors would like to thank T.J. White for helpful discussions concerning crystallinity and photocatalytic measurements.

References

1. H. Wattana, S. Srinivasan, A.G. Sault, and A.K. Datye, *Langmuir*, **12**, 3173 (1996).
2. M.V. Rao, K. Rajeshwar, V.R.P. Verneker, and J. DuBow, *J. Phys. Chem.*, **84**, 1987 (1980).
3. K. Tanaka, W. Luesaiwong, and T. Hisanaga, *J. Mol. Catal. A*, **122**, 67 (1997).
4. J.C. Yu, X. Wang, and X. Fu, *Chem. Mater.*, **16**, 1523 (2004).
5. S. Deki, Y. Aoi, O. Hiroi, and A. Kajinami, *Chem. Lett.*, **433**, 1107 (1996).
6. H. Kishimoto, K. Takahama, N. Hashimoto, Y. Aoi, and S. Deki, *J. Mater. Chem.*, **8**, 2019 (1998).
7. M.-K. Lee, J.-J. Huang, C.-M. Shi, and C.-C. Cheng, *J. Appl. Phys.*, **41**, 4689 (2002).
8. Y. Masuda, S. Ieda, and K. Kounoto, *Langmuir*, **19**, 4415 (2003).
9. N. Ozawa, Y. Kumazawa, and T. Yao, *Thin Solid Films*, **418**, 102 (2002).
10. K. Tanaka, M.F.V. Capule, and T. Hisanga, *Chem. Phys. Lett.*, **185**, 73 (1991).
11. R.L. Sheldrick, *Analytic Profile Fitting of X-Ray Powder Diffraction Profiles in Rietveld Analysis*, edited by R.A. Young (Oxford University Press, 1993), pp. 111–131.
12. G.K.L. Goh, S.K. Donthu, and P.K. Pallathadka, *Chem. Mater.*, **16**, 2857 (2004).
13. J.-G. Yu, H.-G. Yu, B. Cheng, X.-J. Zhao, J.C. Yu, and W.-K. Ho, *J. Phys. Chem. B*, **107**, 13871 (2003).
14. G.K.L. Goh, X.Q. Han, C.P.K. Liew, and C.S.S. Tay, *J. Electrochem. Soc.*, in press (2005).
15. Y. Zheng, E. Shi, Z. Chen, W. Li, and X. Hu, *J. Mater. Chem.*, **11**, 1547 (2001).
16. D. Chen and A.K. Ray, *Water Res.*, **32**, 3223 (2001).