JOURNAL OF MATERIALS SCIENCE **38** (2003) 3069–3072

Synthesis of mesostructured titanium dioxide films by surfactant-templated sol-gel method

N. KITAZAWA, K. SAKAGUCHI, M. AONO, Y. WATANABE
Department of Materials Science and Engineering, National Defense Academy,
1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan
E-mail: nkita@nda.ac.jp

Mesostructured titanium dioxide films have been synthesized by modifying sol-gel methods in the presence of poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) block copolymer surfactants as a structure-directing agent. The synthesized films were analyzed using X-ray diffraction (XRD), field emission transmission electron microscopy (FE-TEM) and selected area electron diffraction (SAED). XRD investigation revealed that as-deposited and as-dried films showed a hexagonal arrangement. With increasing heat-treatment temperature, the mesostructure of the films degraded. From TEM and SAED studies, the degradation of the mesostructure can be explained by the grain growth of microcrystalline titanium dioxide. © *2003 Kluwer Academic Publishers*

1. Introduction

Self-assembly of amphiphilic surfactants has played an important role in the use of sol-gel chemistry for making interesting materials with well-ordered mesostructures. Generally, self-assembly is defined as the spontaneous organization of molecules or polymers *via* noncovalent interactions such as, hydrogen bonding, Van der Waals force, and π-π interaction, without external intervention [1]. Ever since the discovery of the MCM-type mesoporous materials by Mobil researchers [2], considerable attention has been focused on the synthesis and characterization of surfactant-templated mesoporous oxide materials. A variety of mesoporous materials with different compositions and mesostructures have been synthesized in an aqueous solution through co-condensation of inorganic species in conjunction with surfactants [3–6]. However, such materials were made in the form of powder. So far, the processing of mesoporous oxide materials as thin films has been a subject of considerable interest, because thin film materials might offer many opportunities for use in electrical, chemical, optical and mechanical applications [7–9]. Recently, evaporation-induced self-assembly of surfactant during sol-gel thin film processing made it possible to create mesoporous oxide film [1, 10, 11].

Titanium dioxide (TiO_2) is well known not only as a large band-gap semiconductor but also as a photocatalyst material with high efficiency of hydrogen generation under UV-light irradiation [12, 13]. Mesoporous titanium dioxide films with much higher active surface area would yield enhanced photocatalytic efficiency. This article deals with synthesis of mesoporous titanium dioxide films using amphiphilic block copolymers as a structure-directing agent. The synthesized films were characterized by X-ray diffraction (XRD), field emission transmission electron spectroscopy (FE-TEM) and selected area electron diffraction (SAED) patterns.

2. Experimental procedure

Mesoporous titanium dioxide films were prepared by modifying sol-gel methods in the presence of block copolymer surfactants under acidic conditions. Most titanium alkoxides are highly reactive towards hydrolysis and condensation, leading to the formation of uncontrollable precipitates [14]. Therefore, both sols and thin films were prepared in a nitrogen filled grove box.

Reagent grade titanium (IV) butoxide [$Ti(O\text{-}nC_4H_9)_4$, abbreviated as TBOT hereafter, Aldrich], ethyl alcohol (C_2H_5OH, Wako Chemical), hydrochlolic acid (35.5 wt% HCl-aq, Wako Chemical), and distilled water were used for precursor solution preparation. As structure-directing agents, commercially available poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) block copolymers (PEO-PPO-PEO) from BASF were used as follows; Pluronic P65 (average molecular weight, $M_{av} = 3{,}400$), $EO_{20}PO_{30}EO_{20}$; Pluronic P123 ($M_{av} = 5{,}800$), $EO_{20}PO_{70}EO_{20}$. TBOT was added to a mixture of HCl-aq and C_2H_5OH. After 60 min hydrolysis, distilled water and surfactant were added to the sols. Clear and stable sols without any precipitation were obtained when TBOT was hydrolyzed in the presence of a large amount of HCl. The most favorable TBOT:C_2H_5OH:HCl:H_2O molar composition was found to be 1:20:0.75:4 with a surfactant amount of 0.21 to 1.28 g. The sols were then aged under stirring for 24 hrs and finally used for the deposition of films on various substrates [silica glass and Si (100) wafer] using the spin-coating method. During film deposition, the substrate was rotated at 2000 rpm. As-deposited films were dried at 100°C for 12 hrs and then slowly heated (1°C/min) to the 300–600°C thermal range in air to burn out the surfactants and stabilize the structure. The films were kept at the working temperature for 4 hrs and then cooled slowly (1°C/min) to room temperature.

Structural characterization of the films before and after heat-treatment was undertaken using XRD (Rigaku, RINT2000 diffractometer) with Cr K_α radiation (40 kV, 60 mA). FE-TEM observations and SAED pattern measurements were performed using a Hitach; HF-2000 electron microscope operated at 200 kV. For that purpose, thin fragments of the films were scratched from Si (100) substrates and deposited on a cupper grid.

3. Results and discussion

As-deposited, as-dried and calcined films showed smooth surfaces and good transparency. The film thickness of calcined films varied from 1200 to 1500 Å per spin, depending on the surfactant content.

Fig. 1 shows typical X-ray diffraction patterns of as-deposited, as-dried and calcined films prepared from precursor solution with a P123/TBOT weight ratio of 0.50. Note that the calcined film was heat-treated at 400°C for 4 hrs. The as-deposited film shows an intense and narrow Bragg reflection at 1.35° and a much weaker one of 2.69° with d-spacings of 97.2 and 48.8 Å, respectively. The corresponding peaks were indexed as (100) and (200) reflections of a hexagonal structure with an unit cell parameter, $a = 113$ Å. The as-dried film also shows (100) and (200) reflections of a hexagonal structure with $a = 68$ Å. For the calcined film, only one broad peak is observed at 1.74°. Compared with the as-dried film, a decrease in the peak intensity is also noted. Furthermore, the main diffraction peak shifted toward smaller 2θ values with increasing heat-treatment duration. The peak observed for calcined films has not yet been identified at this point, but these results suggest that the degradation of the hexagonal arrangment and further structural transformation might occur upon heat-treatment.

The effects of surfactant content in the sols and heat-treatment temperature on the mesostructure formation were also examined. Fig. 2a shows X-ray diffraction patterns of films deposited from precursor solutions with different P123/TBOT weight ratios and subsequently calcined at 400°C for 4 hrs. X-ray diffraction peak increased in intensity with increasing P123/TBOT weight ratio up to 0.50; afterward, an intensity decrease was observed with further weight ratio increase. Thus, it appears that there is an optimal surfactant content in the sol. Fig. 2b shows XRD patterns of films deposited from a solution with a P123/TBOT weight ratio of 0.50 and subsequently calcined at 400, 450 and 500°C for 4 hrs. The X-ray diffraction peak intensity decreased when increasing the heat-treatment temperature. This can be explained by the disappearance of an ordered structure. Besides, the diffraction peak shifted to larger 2θ values when increasing the heat-treatment temperature.

Fig. 3 shows TEM pictures of the films prepared from precursor solution with a P123/TBOT weight ratio of 0.50 and subsequently calcined at (a) 300, (b) 400, (c) 450 and (d) 500°C for 4 hrs. Corresponding electron diffraction patterns are also shown in each picture. In the TEM pictures, white spots correspond to intergranular pores and black spots correspond to the skeleton of titanium dioxide. The film heat-treated below 300°C

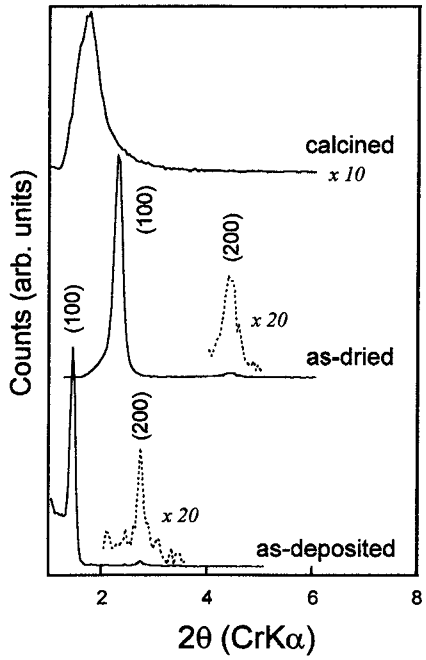

Figure 1 Typical X-ray diffraction patterns of as-deposited, as-dried and calcined films prepared from a precursor solution with a P123/TBOT weight ratio of 0.50. Noted that the calcined film was heat-treated at 400°C for 4 hrs.

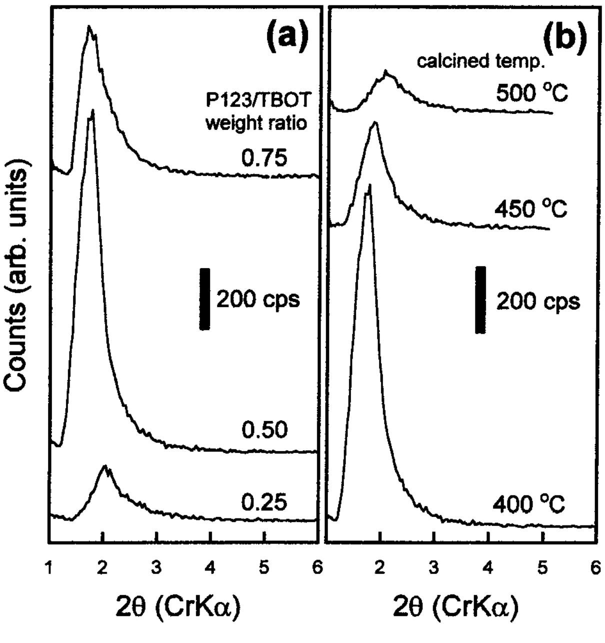

Figure 2 X-ray diffraction patterns of films: (a) prepared from precursor solutions with different P123/TBOT weight ratios and subsequently calcined at 400°C for 4 hrs and (b) prepared from a precursor solution with a P123/TBOT weight ratios of 0.50 and heat-treated at 400, 450 and 500°C for 4 hrs. Note that P123/TBOT weight ratios and calcined temperatures are indicated in each diffraction pattern.

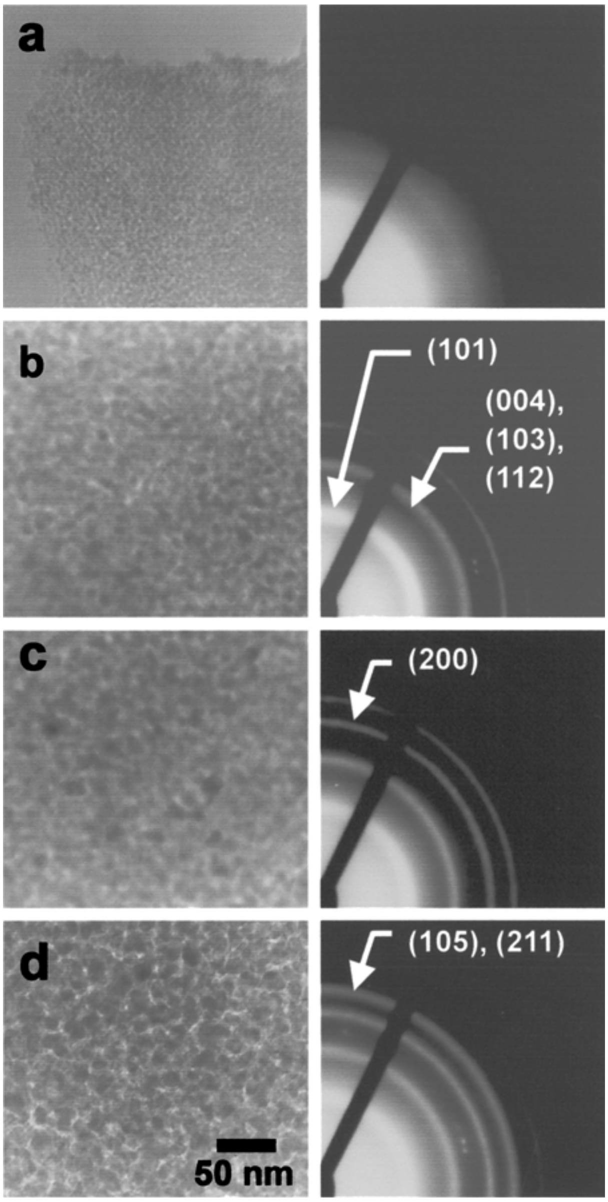

Figure 3 TEM image of films prepared from a precursor solution with a P123/TBOT weight ratio of 0.50 and subsequently calcined at (a) 300, (b) 400, (c) 450 and (d) 500°C for 4 hrs, respectively. Corresponding SAED patterns are also shown in the picture.

(picture a) exhibits disordered pores. From its SAED pattern, the film appears to be amorphous. On the contrary, when the films were heat-treated above 400°C (pictures b, c and d), their SAED patterns showed well defined rings. These diffraction rings were indexed as (101), (004), (103), (112), (200), (105) and (211) reflections of a polycrystalline anatase titanium dioxide. TEM pictures also reveal that the titanium dioxide particles are nanocrystallize. Although the disordered pores still remain in the matrix, the crystallite sizes of the precipitates increased with increasing heat-treatment temperature. From these results, the disappearance of a mesostructure is consistent with the grain growth of titanium dioxide crystallites.

Although the specific mechanism for mesostructure formation in sol-gel thin films is still a subject of discussion, it is generally agreed that evaporation-induced self-assembly stimulates both the formation and ordering of micelles. Usually, surfactants form into micelles with spherical or cylindrical shape in aqueous solution above their critical micelle concentration (*cmc*). These micelles assemble spontaneously into hexagonal, cubic or lamellar phases with further increase of the surfactant concentration in the aqueous solution. In the evaporation-induced self-assembly process using PEO-PPO-PEO block copolymers as a surfactant, homogeneous precursor sols consist of inorganic species, organic solvent, water, acid catalyst and surfactant. In this case, the surfactant concentration in the sols is much weaker than the *cmc*. During thin film processing, preferential evaporation of organic solvent (ethyl alcohol in this study) occurs because of its relatively lower boiling point, which increases the concentration of surfactant as well as water, acid catalyst and inorganic species. Since PEO-PPO-PEO block copolymers consist of hydrophilic PEO blocks and hydrophobic PPO blocks under acidic conditions, inorganic species preferentially interact with the hydrophilic PEO part of the block copolymer *via* both the electrostatic and hydrogen bonding interactions [15]. Further increase in surfactant concentration results in micelle formation and self-assembly in the deposited film. As shown in Fig. 1, the as-deposited and as-dried films showed a hexagonal arrangement, which was modified upon heat-treatment. The mechanism observed here is still unknown at this point, but this can probably be attributed to calcination-induced structural transformation [6]. However, a degradation of the mesostructure occurs in parallel with the crystallization of titanium dioxide (see Fig. 3). To overcome this difficulty, one of the ideas is that porous films with high surface area should be modified by titanium dioxide [16]. In addition, many parameters affect the mesostructure formation induced by this technique: e.g., composition of sol, type of surfactant and its concentration, solvent used, drying process, etc. Therefore a suitable control of these parameters could allow tailoring the structure and pore size.

More detailed study on the synthesis of mesoporous titanium dioxide and titanium dioxide-modified mesoporous silica films are being carried out.

4. Summary

In this study, surfactant-templated mesoporous titanium dioxide films were prepared through sol-gel method, and their structures were investigated by using XRD, TEM and SAED. XRD investigation revealed that the as-deposited and as-dried films showed a hexagonal arrangement, which was modified upon heat-treatment. However, a degradation of the mesostructure was observed when the films were heat-treated at higher temperature. From TEM and SAED studies, degradation of the mesostructure can be explained by the formation and growth of nanocrystalline titanium dioxide.

Acknowledgment

The authors thank BASF (Mt. Olive, NJ) for providing block copolymer surfactants.

References

1. C. J. BRINKER, Y. LU, A. SELLINGER and H. FAN, *Adv. Mat.* **11** (1999) 579.
2. C. T. KRESGE, M. E. LEONOWICZ, W. J. ROTH, J. C. VARTULI and J. S. BECK, *Nature* **359** (1992) 710.
3. Q. HUO, D. MARGOLESE, U. CIESLA, P. FENG, T. G. GIER, P. SIEGER, R. LEON, P. M. PETROFF, F. SCHUTH and G. STUKY, *ibid.* **368** (1994) 317.
4. P. T. TANEV and T. J. PINNAVAIA, *Chem. Mater.* **8** (1996) 2068.
5. D. M. ANTONELLI and J. Y. YING, *ibid.* **8** (1996) 874.
6. P. PUTNAM, N. NAKAGAWA, K. McGRATH, N. YAO, I. AKSAY, S. GRUNER and A. NAVROTSKY, *ibid.* **9** (1997) 2690.
7. S. BASKARAN, J. LIU, K. DOMANSKY, N. KOJLER, X. LI, C. COYLE, G. E. FRYXELL, S. THEVUTHASAN and R. E. WILLIFORD, *Adv. Mat.* **12** (2000) 291.
8. G. WIRNSBERGER, B. J. SCOTT, B. F. CHMELKA and G. D. STUCKY, *ibid.* **12** (2000) 1450.
9. J. A. PAIK, S. K. FAN, C. J. KIM, M. C. WU and B. DUNN, *J. Mater. Res.* **17** (2002) 2121.
10. I. A. AKSAY, M. TRAU, S. MANNE, I. HOMMA, N. YAO, L. ZHOU, P. FENTER, P. EISENBERGER and S. GRYNER, *Science* **273** (1996) 892.
11. Y. LU, R. GANGULI, C. DREWIEN, M. ANDERSON, C. BRINKER, W. GONG, Y. GUO, H. SOYEZ, B. DUNN, M. HUANG and J. ZINK, *Nature* **389** (1997) 364.
12. A. FUJISHIMA and K. HONDA, *Bull. Chem. Soc. Jpn.* **44** (1971) 1148.
13. A. YASUMORI, K. ISHIZU, S. HAYASHI and K. OKADA, *J. Mater. Chem.* **8** (1998) 2521.
14. C. J. BRINKER and G. W. SCHERER (eds.) “Sol-Gel Science” (Academic Press, 1990).
15. B. SMARSLY, C. GOLTNER, M. ANTONIELLI, W. RULAND and E. HOINKIS, *J. Phys. Chem.* B **105** (2001) 831.
16. S. ZHENG, L. GAO, Q. ZHANG and J. GUO, *J. Mater. Chem.* **10** (2000) 723.

Received 11 September 2002
and accepted 14 May 2003