Preparation of Porous Titania Film from Precursor Solution Containing Titanium Alkoxide and Stearic Acid

Shoichi TAKENAKA, Ryoji TAKAHASHI, Satoshi SATO and Toshiaki SODESAWA

Department of Materials Technology, Faculty of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba-shi 263-8522

ステアリン酸を用いた多孔質チタニア薄膜の調製

竹中尚一・高橋亮治・佐藤智司・袖澤利昭

千葉大学工学部物質工学科, 263-8522 千葉市稲毛区弥生町 1-33

A porous titania film was prepared on a glass substrate by a spin-coating technique from the precursor solution containing titanium tetraisopropoxide and stearic acid. Stearic acid formed a 2 : 2 complex with titanium in the dried film, and the complex melted before decomposition. Before the coating of the precursor solution, methylsilane pre-coating on the hydrophilic glass surface was effective in preparing a uniform film because of hydrophobicity of the complex melt. The resultant film was transparent and composed of anatase after heating at 500°C. Micrometer-scale rough surface with aggregates of secondary particles composed of primary crystallites was observed in the film, and mesopores seem to be located at the inter-crystallites. It is probable that decomposition of stearic acid and aggregation of anatase crystallites occur simultaneously to provide the porous structure during heating.

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1. Introduction

Titania (TiO_2) films have created considerable interest for their potential application to wet-type solar cells,¹⁾ photocatalysts for the treatment of polluted water²⁾ and hydrophilic coatings for antifogging mirrors³⁾ since the discovery of strong oxidation and reduction power of photoexcited TiO_2 .⁴⁾ The performance of these devices depends on the surface properties of the films. It is, therefore, important to control the surface structure to enhance the efficiency of the devices. In particular, porous TiO_2 films are required because of their high surface area. Some attempts have been conducted on the preparation of porous TiO_2 films from the precursor solution containing organic polymers.^{5),6)}

We have recently reported that mesoporous TiO_2 with controlled pore size as well as high specific surface area is prepared from complexes of titanium tetraisopropoxide and carboxylic acids.^{7)–9)} The pore size of TiO_2 was controlled from ca. 5 to 20 nm by changing both the molar ratio of carboxylic acid to $\text{Ti}^{7),8)}$ and the alkyl-chain length of carboxylic acid.⁹⁾ The resultant TiO_2 , however, consisted of fine grains of powder. We expect that a film prepared by depositing the mesoporous TiO_2 on a glass substrate shows excellent performance in wide application for its pore structure.

In this research note, we report the preparation of a porous TiO_2 film from the precursor solution containing stearic acid.

2. Experimental

Stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, STA, Wako Pure Chemical Industries, Ltd.) was dissolved in propan-1-ol at 50°C. A mixed solution of titanium tetraisopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$, TTP, Wako Pure Chemical Industries, Ltd.) and propan-1-ol was added to the former solution with vigorous stirring to prepare a clear precursor solution. The molar ratio of TTP, STA and propan-1-ol was 1 : 1.5 : 26. In order to confirm the role of STA, a reference precursor solution without STA was prepared by adding a mixture of H_2O and HNO_3 (60% aqueous solution) dropwise to the TTP-propan-1-ol solution with vigorous stirring. The molar ratio of TTP, propan-1-ol, H_2O and HNO_3 was 1 : 10 : 1 : 0.2.

In this work, the coating procedure was performed by a spin-coating technique at the spinning speed of 2000 rpm for 20 s at room temperature. Each precursor solution was coated on a borosilicate glass substrate ($18 \times 32 \times 0.12$ – 0.17 mm) which had been washed with propan-1-ol and had been heated at 400°C for 10 min. The coating film was dried at 50°C for 30 min and heated at 500°C for 1 h at the heating rate of 50°C h⁻¹ to decompose organic residuals. In some case, a methylsilane solution was coated on the substrate before the coating of the precursor solution containing STA. The pre-coating solution was prepared by partial hydrolysis of methyltrimethoxysilane ($\text{Si}(\text{OCH}_3)_3\text{CH}_3$, MTMS, Shin-Etsu Silicon Chemicals) with acidified water at room temperature. The molar ratio of MTMS, methanol and H_2O in 1 mol dm⁻³ HNO_3 was 1 : 4 : 1. The methylsilane-coated substrate was dried at 50°C for 30 min before the coating of the precursor solution.

Surface morphology of the TiO_2 films was observed by a scanning electron microscope (SEM; ABT-32T, Topcon), an atomic force microscope (AFM; SPA400, Seiko Instruments Inc.) and a field emission scanning electron microscope (FE-SEM; S-4700, Hitachi). Optical transmittance of the TiO_2 films was measured using an ultraviolet-visible spectrophotometer (UV-1600PC, Shimadzu). X-ray diffraction (XRD) patterns were recorded on an M18XHF (Mac Science) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154$ nm) to investigate the crystal structure of the TiO_2 films.

3. Results and discussion

Figure 1 shows a SEM micrograph of a TiO_2 film prepared by coating the precursor solution containing STA on the substrate without the methylsilane pre-coating. Many hemispherical islands with diameter of 20 to 100 μm are randomly distributed on the substrate. The film dried at 50°C comprises a complex of TTP and STA, and the complex melts during heating. Because of hydrophobicity of the complex melt, the film is dotted with many droplets, and the island structure is formed after heating at 500°C. It is clear that hydrophobicity of STA is disadvantageous for preparing a uniform TiO_2 film on hydrophilic glass surface. To solve this problem, the partially hydrolyzed MTMS solution

Fig. 1. SEM micrograph of a TiO_2 film prepared with STA. No precoating of MTMS solution was performed on the substrate before the coating of the precursor solution. The image was observed from the tilt angle of 70° .

was coated on the substrate to prepare hydrophobic surface with Si-CH_3 . A uniform TiO_2 film was prepared by coating the precursor solution containing STA on the methylsilanized substrate. A uniform TiO_2 film was also prepared by coating the precursor solution without STA on non-methylsilanized substrate.

The XRD peaks of anatase TiO_2 were observed for the TiO_2 films prepared with and without STA after heating at 500°C (patterns not shown). The TiO_2 films were highly transparent and interference fringes were observed in the optical transmission spectra. (spectra not shown).

Figure 2 shows AFM images of the TiO_2 films. The substrates are slightly curved because of deformation of thin glass plate by heating at 500°C . The TiO_2 film prepared without STA (Fig. 2(a)) has fairly smooth surface. Surface of the TiO_2 film prepared with STA (Fig. 2(b)) is much rougher than that of the TiO_2 film prepared without STA. The rough surface consists of large circular concaves whose size is ca. $1\ \mu\text{m}$ and small irregular convexes whose size is

$<1\ \mu\text{m}$. We have previously reported that fine grains of TiO_2 powder prepared with STA consist of anatase crystallites whose diameter is ca. $10\ \text{nm}$, and that mesopores whose size is in the range of $5\text{--}15\ \text{nm}$ are located at the inter-crystallites.⁸⁾ It is clear that the size of the concaves observed in the AFM image is much larger than that of the mesopores observed in the powder samples. Further investigation of surface structure of the TiO_2 film was carried out by FE-SEM.

Figure 3 shows FE-SEM micrographs of the TiO_2 film prepared with STA. Rough surface structure with aggregates of particles whose diameter is ca. $1\ \mu\text{m}$ is observed, and macropores whose size is ca. $0.5\ \mu\text{m}$ are located at the interparticles (Fig. 3(a)). Each particle seems to be a secondary particle composed of smaller primary particles whose diameter is several tens nanometers (Fig. 3(b)). The primary particles probably correspond to the crystallites observed in the powder samples in the previous work.⁸⁾ If this consideration is correct, we can conclude that the porous structure of the TiO_2 film is essentially the same as that of the powder samples.

The porous structure of the TiO_2 film prepared with STA is considered to be a result of the removal of STA. In the TiO_2 film prepared without STA, the film crystallizes gradually and becomes dense structure because of growth and coalescence of crystallites during heating. In the TiO_2 film prepared with STA, decomposition of STA and aggregation of anatase crystallites occur simultaneously to provide the pore structure. The TiO_2 film showed substantial mechanical strength against a simple scratch test in spite of the rough surface structure. This method can be a new technique for preparing porous films.

4. Conclusion

A porous anatase TiO_2 film was prepared by coating the precursor solution containing STA on methylsilanized glass substrate. During heating, STA was removed to provide the porous structure, and the film crystallized to anatase. The TiO_2 film was transparent after crystallization in heating at 500°C . The transparent anatase film with porous structure is expected to show excellent performance in wide application.

Fig. 2. AFM images of the TiO_2 films prepared (a) without STA and (b) with STA.

Fig. 3. FE-SEM micrographs of the TiO_2 film prepared with STA. The images were observed at different magnification: (a) $\times 10000$ and (b) $\times 100000$.

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References

- 1) O' Regan, B. and Gratzel, M., *Nature*, **353**, 737–39 (1991).
- 2) Matthews, R. W., *J. Phys. Chem.*, **91**, 3328–33 (1987).
- 3) Wang, R., Hashimoto, K., Fujishima, A., Chikuni, M., Kojima, E., Kitamura, A., Shimohigoshi, M. and Watanabe, T., *Nature*, **388**, 431–32 (1997).
- 4) Fujishima, A. and Honda, K., *Nature*, **238**, 37–38 (1972).
- 5) Kato, K., Tsuzuki, A., Torii, Y., Taoda, H., Kao, T. and Butsugan, Y., *J. Mater. Sci.*, **30**, 837–41 (1995).
- 6) Kajihara, K., Nakanishi, K., Tanaka, K., Hirao, K. and Soga, N., *J. Am. Ceram. Soc.*, **81**, 2670–76 (1998).
- 7) Sato, S., Oimatsu, S., Takahashi, R., Sodesawa, T. and Nozaki, F., *Chem. Commun.*, 2219–20 (1997).
- 8) Takahashi, R., Takenaka, S., Sato, S., Sodesawa, T., Ogura, K. and Nakanishi, K., *J. Chem. Soc., Faraday Trans.*, **94**, 3161–68 (1998).
- 9) Takenaka, S., Takahashi, R., Sato, S. and Sodesawa, T., *J. Sol-Gel Sci. Technol.*, **19**, 711–14 (2000).