Effects of Annealing on the Morphology and Porosity of Porous TiO₂ Films Fabricated by Deposition of Aerosol Nanoparticles

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The present study investigates the impact of post annealing of TiO₂ nanoparticulate films on their crystallinity, mechanical strength, and morphology. Non-agglomerated and amorphous TiO₂ nanoparticles of 46 nm diameter were synthesized in a plasma field, and were subsequently deposited on substrates to form nanoparticulate films. The films were annealed at various temperatures in the range of 100–1,200°C. Phase transformations from amorphous-to-anatase and from anatase-to-rutile were observed at 400°C and at 1,000°C, respectively. The high rutile transformation temperature was considered to be due to a tensile field induced by shrinkage of the film. The as-deposited film and the films annealed at below 400°C had poor mechanical strength. Conversely, the films annealed at over 500°C were strengthened by necking of the nanoparticles. The size of nanoparticles changed with increasing temperature. Annealing at 100–300°C caused the nanoparticles to shrink to approximately 30 nm. The nanoparticle diameters changed only slightly when annealed at 400–600°C because the annealing time was insufficient for changes to manifest. Annealing at 700–900°C caused the nanoparticle diameter to increase to approximately 50 nm because of sintering and coalescence of the nanoparticles. The diameter of the nanoparticles annealed at over 1,000°C became approximately 200 nm because of densification during the anatase-to-rutile transformation. The porosities of the films annealed at below 900°C were over 80%. However, the porosities of the films annealed at over 1,000°C decreased significantly due to densification.

Introduction

Porous thin films exhibit a wide range of interesting characteristics, such as optical properties, electrical conductivity, and thermal resistance (Choy, 2003). They have been exploited for use in gas sensors (Shishiyani *et al.*, 2005; Wang and Shadman, 2013), photocatalysts (Cao *et al.*, 2005; Wu *et al.*, 2011), and dye sensitized solar cells (DSSCs) (Yum *et al.*, 2005; Zhang *et al.*, 2009). The performance of these devices is determined by the crystallinity and the porosity of the films. For example, a gas sensor requires high crystallinity of the constituents of the films (Tiemann, 2007) while the performance of DSSCs is related to the porosity of the films (Tricoli *et al.*, 2012). Thus, it is important to control the porosity and the crystallinity of porous films when they are prepared.

There are a number of methods for the preparation of porous films, which are classified broadly into two categories: liquid-phase and gas-phase syntheses. One example of liquid-phase synthesis involves the precursors of the film being self-assembled with template agents on a substrate (Brinker *et al.*, 1999). After removal of the templates, the film possesses a highly uniform porous structure. However, this method has concerns regarding composition limitations and process complexities. Another example is the deposition

of colloidal nanoparticles onto the substrate by, for example, liquid coating or inkjet printing (Yum *et al.*, 2005; Merrill and Sun, 2009). Because there are many kinds of colloidal nanoparticles, this process can facilitate porous films fabricated from many compositions. However, this method also has concerns regarding the contamination of the solvent and/or the dispersing agent.

In many cases, dry processes in the gas phase—as represented by flame spray pyrolysis (FSP), chemical vapor deposition (CVD), and plasma-enhanced CVD (PECVD)—are considered suitable for the preparation of porous films with high purity. The porous films fabricated by these methods are constructed from the deposition of the nanoparticles synthesized in gas phase. FSP is a common technique for the preparation of nanoparticles, which is widely used in both academic research and industrial manufacturing (Pratsinis, 2010). FSP has also been applied to fabricate porous films by the deposition of several types of nanoparticles (Mädler *et al.*, 2006; Tricoli *et al.*, 2008; Tricoli *et al.*, 2012). CVD processes that enable the generation of nanoparticles in the gas phase have also been used for the preparation of nanoparticulate films. Nolan *et al.* (2006) fabricated nanoparticulate films by the deposition of TiO₂ nanoparticles synthesized by CVD. Although the films fabricated by FSP and CVD have very high porosities, the pore structures are not uniform because the nanoparticles tend to agglomerate. Thus, non-agglomerated nanoparticles are sought to achieve both high porosity and a uniform pore structure.

In a previous study, we synthesized non-agglomerated nanoparticles by PECVD (Hayashi *et al.*, 2008) where the

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negative charge of the particles formed in the plasma caused mutual electrostatic repulsion and prevented their agglomeration. In addition, we succeeded in the preparation of porous TiO₂ film using the non-agglomerated nanoparticles (Kubo *et al.*, 2013). The pore structures of the film could be tuned by the diameters of the nanoparticles and deposition velocities. However, the nanoparticulate films suffered from low mechanical strength and the nanoparticles were amorphous TiO₂, which resulted in them being inefficient in applications such as gas sensors, photocatalysts, and DSSCs. Annealing and subsequent sintering of the nanoparticles is one option for enhancing mechanical strength and crystallinity. Annealing of TiO₂ nanoparticles films at 450°C resulted in strong adhesion at the interface between the nanoparticles and the substrate (Pichot *et al.*, 2000). Wu *et al.* (2011) reported that annealing of the amorphous TiO₂ films synthesized by PECVD resulted in the crystallization of TiO₂ to the anatase phase and the enhancement of photocatalytic activity. Besides, the morphology of the films is considered to be controlled by the annealing process because of sintering of the nanoparticles, enabling the films to be optimized for specific applications. We, therefore, investigated the impact of post annealing of nanoparticulate films—which were fabricated by the deposition of non-agglomerated TiO₂ nanoparticles synthesized in the plasma field—on their crystallinity, mechanical strength, and morphology. The details of the sintering process of TiO₂ nanoparticle were also investigated.

1. Experimental

Nanoparticulate films were fabricated using a plasma reactor and a deposition chamber. The complete details of the apparatus are described in our previous work (Kubo *et al.*, 2013). A brief description of the apparatus is as follows: the plasma reactor had a coaxial bicylindrical structure, consisting of a stainless steel outer cylinder covered with an electrically grounded Cu sleeve and a stainless steel inner rod coupled to a radio frequency (RF) power supply (AX-1000IIP, Adtec Plasma Technology Co., Ltd.). These two cylinders, i.e. electrodes, were approximately 22.3 mm apart. An RF power of 100 W at 13.56 MHz was applied to the inner electrode through a matching network. The deposition chamber connected to the plasma reactor consisted primarily of a stainless steel cylinder, with a circular inlet of 10.5 mm diameter. In this design, a substrate was positioned 20.9 mm from the inlet of the deposition chamber. The substrate was a square Si[100] wafer (10 mm×10 mm), mounted onto a cylindrical copper block electrode and connected to a DC power supply.

Titanium tetraisopropoxide (TTIP) was used for the synthesis of TiO₂ nanoparticles by the plasma reaction of the metal-organic precursors. To vaporize TTIP, argon was bubbled as the carrier gas at a flow rate of 0.935 sccm and temperature of 40°C, and delivered to the plasma reactor. Argon gas was also fed into the reactor for dilution of TTIP at a flow rate of 293 sccm. The total pressure in the reactor was

0.743 kPa. The synthesized nanoparticles and argon gas were fed continuously into the deposition chamber for 5 min to allow deposition onto the substrate, to which a bias voltage of +400 V was applied to deposit nanoparticles uniformly. The fabricated nanoparticulate films were annealed in an air atmosphere at 100–1,200°C for 12 h with heating and cooling rates of 5 K min^{−1} at the start and end of the annealing process, respectively.

The surface and cross-sectional morphologies of the porous films prepared by deposition were examined using a scanning electron microscope (SEM, S-5200, Hitachi High Technologies Corp.). From the SEM images, the geometric mean diameter (GMD) of the nanoparticles were measured. Particle diameter, d_p , was measured for more than 300 particles from SEM images. GMD was calculated by Eq. (1).

$$\log(\text{GMD}) = \frac{\sum_i^n \log d_{pi}}{n} \quad (1)$$

Here, n is the total number of measured particles and d_{pi} denotes the diameter of i -th particle. The geometric mean pore size of the nanoparticulate films was also estimated by Eq. (1) in which d_p and GMD were replaced by pore size and geometric mean pore size, respectively. Powder X-ray diffraction (XRD) measurements were performed using an RINT2100 (Rigaku Corp.) equipped with a CuK α radiation source. Crystal grain sizes were calculated on the basis of XRD line broadening using Scherrer's equation given as Eq. (2).

$$D = \frac{K\lambda}{B \cos \theta} \quad (2)$$

Here, D is the average nanocrystalline size, K is a constant (here, a value of 1.38 was assumed (Winardi *et al.*, 2010)), λ is the wavelength of the CuK α line ($= 1.5406 \text{ \AA}$), B is the full width at half maximum which was obtained by subtracting the system value from the measured value, and θ is the peak angle. Raman spectroscopies were performed using a Horiba JY T64000 micro-Raman spectrometer (Horiba Ltd.) (excitation line was 514.5 nm). Fourier-transform infrared (FT-IR) spectra of the samples were obtained on a NICOLET iS10 (Thermo Scientific Inc.) with a nominal resolution of 2 cm^{−1}.

2. Results

The XRD patterns of the TiO₂ nanoparticulate films annealed at various temperatures are shown in **Figure 1**. The patterns of the as-deposited film and the films that were annealed at below 300°C exhibit no diffraction peak, indicating that the nanoparticles synthesized by the present PECVD were amorphous. The peaks attributed to the anatase phase were observed with annealing temperatures from 400 to 900°C. The crystal sizes for the different annealing temperatures, as calculated by Eq. (2) and shown in the inset of **Figure 2**, were 23 nm for 400°C, 25 nm for 500°C, 28 nm for 600°C, 37 nm for 700°C, and 49 nm for 800°C. These

Fig. 1 XRD patterns of TiO₂ nanoparticulate films annealed at various temperatures

Fig. 2 GMD of the nanoparticles consisting the films (circle) and crystal sizes estimated from XRD patterns (triangle); inset is a magnification of the annealing temperature range below 1,000°C

values are consistent with the GMDs of the nanoparticles estimated from SEM images as described later. At an annealing temperature of 1,000°C, the intensity of the (101) plane at $2\theta = 25.4^\circ$ decreased compared to that observed at 900°C, and a peak at $2\theta = 27.2^\circ$ appeared. This peak was attributed to the (110) plane of the rutile phase, indicating that the phase transformation from anatase to rutile was initiated by annealing at 1,000°C. The anatase (101) peak at $2\theta = 25.4^\circ$ and the rutile (110) peak at $2\theta = 27.2^\circ$ were analyzed to evaluate the weight fraction x of the rutile phase using Eq. (3) (Hanaor and Sorrell, 2011).

$$x = \frac{1}{1 + 0.8 \left(\frac{I_A}{I_R} \right)} \quad (3)$$

Here, I_R and I_A are the intensities of the rutile (110) peak and the anatase (101) peak, respectively. The rutile fraction was estimated to be 86%. By further increasing the annealing temperature over 1,100°C, the films exhibited only the peaks attributed to rutile phase.

The films' phase transformations caused by annealing

Fig. 3 Raman spectra of TiO₂ nanoparticulate films annealed at various temperatures

were also confirmed by Raman spectra, as shown by the significant spectra of the annealed films in Figure 3. In all of the spectra, a peak at 520 cm⁻¹ was detected, which was attributed to the Si substrate (Parker *et al.*, 1967). The spectrum of as-deposited film exhibited only the 520 cm⁻¹ peak, indicating that the TiO₂ nanoparticles were amorphous. The amorphous structures were observed for the films annealed at temperatures below 300°C. At 400°C, three small peaks at 142, 393, and 636 cm⁻¹ appeared which were attributed to the anatase phase (Busca *et al.*, 1994). The intensities of the peaks increased with annealing temperature. Even higher annealing temperatures resulted in phase transformation to the rutile phase, as revealed by the three peaks at 234, 444, and 608 cm⁻¹. At an annealing temperature of 1,000°C, a small peak was observed at 142 cm⁻¹, which was attributed to the anatase phase. The rutile fraction, estimated by the area ratios of the peak at 142 cm⁻¹ for anatase phase to the peak at 445 cm⁻¹ for rutile phase (Zhang *et al.*, 2006), was 87%, which is in good agreement with that estimated from the XRD patterns.

Figure 4 shows the SEM images of the films fabricated by the deposition of TiO₂ nanoparticles before and after annealing. Before annealing, the GMD of the deposited nanoparticles was 46 nm. The geometric mean pore size and the film thickness measured from the SEM images were 0.12 and 19.2 μm, respectively. The GMDs of the nanoparticles of the films annealed at various temperatures are shown in Figure 2. After annealing at 100°C, the GMD of the particles decreased to 25 nm. In annealing temperatures in the range 100–600°C, the GMDs changed only slightly. However, annealing at 700–900°C enlarged the GMDs of the nanoparticles to 50 nm, and annealing at over 1,000°C enlarged the GMD significantly.

The pore sizes that were estimated from the SEM images are summarized in Figure 5. The geometric mean pore size increased as the annealing temperature increased with pore sizes of approximately 0.15–0.3 μm. Increasing the annealing temperature over 1,000°C resulted in large pore sizes of over 1 μm.

The porosities of the films were estimated by the film

Fig. 4 SEM images of the cross-section of the as-deposited film and for films annealed at various temperatures; (a) as-deposited, (b) 100°C, (c) 200°C, (d) 300°C, (e) 400°C, (f) 500°C, (g) 600°C, (h) 700°C, (i) 800°C, (j) 900°C, (k) 1,000°C, (l) 1,100°C, and (m) 1,200°C; the insets are magnified images

Fig. 5 Geometric mean pore size of the films; inset is magnification of the temperature range below 900°C

thickness (Mädler *et al.*, 2006; Kubo *et al.*, 2013). When a porous film of apparent thickness s is transformed into a dense film of thickness s_{bulk} , the porosity of the original film (ρ) is estimated by Eq. (4).

$$\rho = 1 - \frac{s_{\text{bulk}}}{s} \quad (4)$$

The film that was annealed at 1,250°C for 30 h was a dense TiO_2 film with a thickness of 1.7 µm and without pores. We used Eq. (4) to estimate the porosity of the film under the assumption that the loss and density change of the film materials are negligible. Before annealing, the film had a large porosity of 91% and after annealing at temperatures below 900°C, the porosities remained at over 80%. However, when the annealing temperature was increased above 1,000°C, this

Fig. 6 Film porosity estimated from the film thickness; inset is the film thickness

resulted in thinning of the films, as shown in Figures 4(k) to (m), which caused a decrease in the film porosity.

The mechanical strength of the annealed films was examined by immersing the films into water for 24 h. **Figure 7** shows the SEM images of the annealed films after immersion. For the as-deposited film and the films annealed at 100 and 200°C, immersion in water collapsed their structures with the majority of the particulate films being detached, leaving discontinuous nanoparticles layers on the substrates. **Figure 8** shows the GMDs of the nanoparticles in the films after immersion and that the GMD of the nanoparticles increased after immersion. Annealing at 300 and 400°C allowed the film to keep its structure, while the GMD of nanoparticles also increased. In addition, the film thickness was thinner compared to that before immersion. For

Fig. 7 SEM images of top-view (a)–(c) and cross-sectional view (d)–(f) of the annealed nanoparticulate films after being immersed in water; the insets in (d)–(f) are magnified images

Fig. 8 GMDs of nanoparticles before (circle) and after (square) immersion in water

the films annealed at over 500°C, the morphology and the GMDs of the nanoparticles were not affected by immersion.

3. Discussion

Annealing of the nanoparticulate films simultaneously affected the film morphologies and the crystallinities. Morphological factors—such as nanoparticle size, pore size, and porosity—displayed a similar trend with changing annealing temperature. Table 1 summarizes the results of the annealing for the crystal phase, GMD of nanoparticles, crystal size of anatase, porosity, film thickness, and geometric mean pore size. Transformations of the morphologies and crystallinities were considered to proceed according to the following four stages: i) shrinkage of nanoparticles (as-deposited to 300°C); ii) phase transformation from amorphous to anatase with constant particle diameter (400–600°C); iii) sintering of anatase particles (700–900°C); and iv) phase transformation from anatase to rutile (over 1,000°C). A schematic illustration of the transformation is shown in Figure 9.

i) Shrinkage of nanoparticles (as-deposited to 300°C)

After annealing at 100–300°C, the GMD of the nanoparticles decreased from 46 nm to 25–30 nm. The shrinkage of the nanoparticles is not fully understood; however, one pos-

sibility is the densification of each particle by dehydration of the residual hydroxyl groups by annealing. FT-IR analysis (data not shown) revealed that the film possessed hydroxyl groups before undergoing the annealing process. On the other hand, the hydroxyl groups were not observed after annealing at 100°C. It indicates that dehydration occurred. The shrinkage of the particles would be due to the release of water by dehydration (Rubio *et al.*, 1997). Conversely, immersion of the films in water enlarged the nanoparticles. This enlargement would be due to rehydration of Ti–O–Ti bonding to Ti–OH groups.

The macroscopic morphologies of the films also changed with annealing temperature. The films annealed at 100–300°C were thinner than the as-deposited film (Figure 6). Because the degree of the film thinning (20–40%) was approximately consistent with the degree of the diameter shrinkage (30–40%), the decrease of the film thickness was considered to be caused by the decrease in the constitutive nanoparticles' diameter.

ii) Phase transformation from amorphous to anatase with constant particle diameter (400–600°C)

The phase transformation from the amorphous to the anatase phases was initiated by annealing at 400°C, as is consistent with previous works (Wu *et al.*, 2011). The crystal sizes estimated from the XRD pattern were in good agreement with the GMDs estimated from the SEM images, which indicated that the individual nanoparticles were transformed into anatase nanocrystals. The nanoparticles annealed at 500°C had rigid molecular skeletons due to the phase transformation, which might prevent the swelling of the nanoparticles when immersed in water. In addition, neck growth of the interfaces of the nanoparticles, caused by sintering, is considered to have strengthened the particle network.

Little change was observed in the diameter of the nanoparticles and their porosities when the annealing temperature was increased from 400 to 600°C. A lack of observed change in the nanoparticle diameter was considered to be caused by insufficient annealing time for sintering to

Table 1 Summary of the structural parameters of the films after annealing

Annealing temperature [°C]	Crystal phase	GMD (geometric mean diameter) of nanoparticles [nm]	Crystal size of anatase [nm]	Porosity [—]	Film thickness [μm]	Geometric mean pore size [μm]
As-deposited	Amorphous	46	—	91	19.2	0.12
100	Amorphous	25	—	89	15.5	0.15
200	Amorphous	30	—	85	11.6	0.14
300	Amorphous	27	—	85	11.1	0.20
400	Anatase	29	23	87	13.3	0.17
500	Anatase	26	25	87	12.5	0.22
600	Anatase	25	28	86	12.0	0.21
700	Anatase	37	37	82	9.2	0.29
800	Anatase	45	49	87	13.2	0.26
900	Anatase	47	—	83	9.7	0.31
1,000	Anatase/Rutile	200	—	59	4.1	0.90
1,100	Rutile	560	—	47	3.2	1.21
1,200	Rutile	1,400	—	9	1.8	1.52

Fig. 9 Schematic illustration of the transformation of the film morphology

occur, as discussed further below.

iii) Sintering of anatase particles (700–900°C)

The GMDs and crystal size of the nanoparticles increased when the annealing temperature was increased from 700°C. The increase in the size of the nanoparticles was considered to be caused by their sintering. As sintering is considered to be governed by a surface diffusion model, the characteristic time for sintering, τ , of TiO₂ particles is given by Eq. (5) (Nakaso *et al.*, 2001).

$$\tau [\text{s}] = 7.44 \times 10^{16} [\text{sm}^{-4} \text{K}^{-1}] d_p^4 [\text{m}] T [\text{K}] \times \exp \left(\frac{2.58 \times 10^5 [\text{kJ}]}{RT} \right) \quad (5)$$

Here, d_p is the particle diameter, T is the temperature, and R is the universal gas constant. τ for TiO₂ nanoparticles of 30 nm in diameter (the initial diameter of the 46-nm nanoparticles after heating at 100–300°C) was calculated to be 39 h for 600°C and 1.1 h for 700°C. This means that the annealing time of 12 h was insufficient for the nanoparticles to be sintered at 600°C, but was sufficient at 700°C, which resulted in the increase of the diameter of the nanoparticles at the higher annealing temperature. At even higher an-

nealing temperatures (800 and 900°C), further sintering occurred and larger GMDs of nanoparticles resulted.

The films annealed at 700–900°C had almost the same thicknesses as the film annealed at 600°C, even though the GMD of particles increased. To explain this, we considered that the nanoparticulate network had two roles in constructing the film's morphology: one as forming the main framework of the film structure, and the other as forming side chains (**Figure 10**). Sintering causes the nanoparticles in the side chains to coalesce with the main framework, while the nanoparticles of the main framework maintain the film structure. As a result, the pore sizes of the films annealed at 700–900°C were larger than those in the film annealed at 600°C, but the thicknesses of the films did not appreciably change.

iv) Phase transformation from anatase to rutile (over 1,000°C)

The crystalline phase of the nanoparticles was transformed from anatase to rutile at 1,000°C. This temperature is considerably higher than that expected for the anatase nanoparticles of 30–50 nm in diameter as the transformation temperature has generally been reported to be approximately 600°C for powder anatase nanoparticles of diameter

Fig. 10 Schematic illustration of film sintering without change of film thickness

larger than 14 nm (Zhang and Banfield, 1998; Hanaor and Sorrell, 2011). However, some investigations of the annealing effects on the transformation of TiO_2 films fabricated by sputter deposition (Wiggins *et al.*, 1996), MOCVD (Won *et al.*, 2001), and sol-gel dip-coating (Kim *et al.*, 2002) reported that the transformation temperatures exceeded 600°C. Kumar *et al.* (1993) investigated the difference in the transformation temperature between nanoparticle powder and nanoparticulate films both synthesized by the sol-gel method. The transformation temperature of the film was higher than that of powder. They considered that the film experienced a two-dimensional tensile stress field, which would be caused by shrinkage perpendicular to the substrate. The tensile stress would increase the total Gibbs free-energy change in the crystalline phase transformation, and as a result the anatase-to-rutile transformation of the films, required a higher annealing temperature. In a similar manner, the high transformation temperature of 1,000°C from anatase to rutile of the film was attributed to the tensile field in the shrinking film. In this fourth stage, the size of the particles and the thickness of the film significantly changed. The increase in the particle size was caused by the anatase-to-rutile transformation (Edelson and Glaeser, 1988; Hague and Mayo, 1993). During or after the transformation, rutile particles were sintered to become large particles. The sintering of the rutile particle collapsed the porous structure of the film and resulted in the decrease of the film thickness. Even higher annealing temperature caused further sintering, which resulted in further densification of the film.

Conclusion

The effects of post annealing of the nanoparticulate films at various temperatures on their crystallinity, mechanical strength, and morphology were investigated. The transformation of the morphologies and crystallinities were considered to comprise four stages: shrinkage of nanoparticles; amorphous-to-anatase transformation; sintering of nanoparticles; and anatase-to-rutile transformation. We controlled the porous structure and the crystal phase of the films by changing the post-annealing temperature. Furthermore, the anatase phase, which has a higher photocatalytic

activity than the rutile phase, was maintained even after annealing at 900°C. The photocatalytic activities of the films annealed at various temperatures are under investigation.

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Nomenclature

B	= full width at half maximum (fwhm) of XRD pattern peak	[rad]
D	= average nanocrystalline size	[m]
d_p	= diameter of particle	[m]
I_A	= intensities of the anatase (1 0 1) peak of XRD pattern	[—]
I_R	= intensities of the rutile (1 1 0) peak of XRD pattern	[—]
K	= constant for Scherrer's equation	[—]
R	= universal gas constant	[J K ⁻¹ mol ⁻¹]
s	= film thickness	[m]
s_{bulk}	= bulk film thickness	[m]
T	= temperature	[K]
x	= weight fraction of rutile	[—]
λ	= wavelength of the $\text{CuK}\alpha$ line	[m]
ρ	= porosity	[—]
τ	= characteristic time for sintering	[s]
θ	= peak angle of XRD pattern	[rad]

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