Water-assisted crystallization and densification of sol–gel-derived TiO$_2$ films during low-temperature heating

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ABSTRACT
The crystallization and densification behavior of TiO$_2$ films during heating at below 400°C was studied for sol–gel coatings and the effect of the H$_2$O content in the precursor solutions on the nucleation and crystal growth of anatase at such relatively low temperature was discussed. TiO$_2$ gel films were prepared from Ti(OC$_3$H$_7$)$_4$:HNO$_3$:H$_2$O:Ti(OH)$_2$:H$_2$O solutions, followed by heating at 200–400°C for 10 min–6 h in air, where the H$_2$O/Ti(OC$_3$H$_7$)$_4$ mole ratio ($x$) was varied from 1.0 to 8.0. The degree of crystallization and the crystallite size of the heat-treated TiO$_2$ films were not significantly affected by the H$_2$O content, while the surface structure became denser with an increase in $x$. The dense TiO$_2$ films of $x = 8.0$ heated at 300–400°C for 6 h exhibited a refractive index of 2.22–2.25, which was higher than that of $x = 1.0$ heated at 800°C.

1. Introduction
Because of their high refractive index and the high transparency in the visible range, titania (TiO$_2$) film materials are widely used for many optical applications, such as antireflective coatings [1–3], optical waveguides [4,5], and microlens arrays [6,7]. The sol–gel process is a typical coating method for providing uniform TiO$_2$ layers on various substrates, where amorphous gel films are made from titanium alkoxide solutions containing water, acidic or basic catalysts, and alcoholic solvents, and then thermally converted to polycrystalline TiO$_2$ films. Sol-gel coating techniques allow us to easily and economically control the thickness and chemical composition of metal oxide thin films on any substrates [8–10]. Additionally sol-gel-derived coating layers are known to be crystallized at relatively low heating temperature [10]. The crystallinity, crystallite size, and microstructure of the resultant TiO$_2$ films are significantly influenced by the hydrolysis and condensation reactions of metal alkoxides [11–17], and thus the composition of the coating solutions is an essential factor for controlling the performance of the devices.

Our research group has focused on the crystallization and densification of TiO$_2$ materials prepared in the presence of a large amount of water. For the crystallization of glass materials, water molecules and OH groups in the glass matrix were reported to act as the source of oxygen and reduce the viscosity of the glass, increasing the crystal nucleation and growth rates [18,19]. The crystallization promoted by water has also been reported for TiO$_2$ materials, where the hydrogen bonding by water molecules between the surface OH groups of TiO$_6$ octahedra are thought to make the intermediate structures suitable for the transformation into the face-sharing anatase structure.
2. Experimental

Starting materials of Ti(O(C2H5)4)4, HNO3 (69 mass%), and C2H5OH were purchased from Wako Pure Chemical Industries, Osaka, Japan. Coating solutions with molar compositions Ti(O(C2H5)4)4H2O:HNO3:C2H5OH = 1:x:y:10 (x = 1.0 and y = 0.6, or x = 8.0 and y = 1.0) were prepared by the following procedure. Ti(O(C2H5)4)4 was added to a half of the prescribed amount of C2H5OH solvent. The remaining C2H5OH was mixed with purified water and nitric acid, and then the mixed solution was added dropwise to the Ti(O(C2H5)4)4 solution under stirring in an ice-water bath. After stirring in the ice-water bath for 30 min and then at room temperature for 30 min, the resultant solutions were served as coating solutions.

Precursor gel films were prepared by dip-coating at a substrate withdrawal speed of 5.0 cm min⁻¹ on silica glass (20 mm × 40 mm × 0.85 mm) or Si(100) substrates (20 mm × 40 mm × 0.5 mm). The gel films were immediately transferred to an electric furnace held at 200–400°C, before being kept at prescribed temperatures for 10 min–6 h, then taken out of the furnace to the ambient atmosphere. All the heat-treatment processes were carried out in air.

The thickness and refractive index of the films were evaluated with a spectroscopic ellipsometer (M-2000 V-Kk, J.A. Woollam Company, Nebraska, USA) at three angles of incidence of 65°, 70°, and 75° over the spectral range 370–1000 nm. The crystalline phases were measured by X-ray diffraction (XRD; Model Rint 2550, Rigaku, Tokyo, Japan) using the ordinary 2θ/θ mode, where the measurement was performed with CuKa radiation operated at 40 kV and 300 mA. The valance state of Ti⁴⁺ species in the product films were obtained using an X-ray photoelectron spectrometer (XPS; PHI5000 Versa Probe, ULVAC-PHI, Chigasaki, Japan) with a monochromatic AlKa X-ray source. To counter the surface charging, a charge neutralizer was used during the collection of the spectra. The microstructure of the thin film samples was observed using a scanning probe microscope (SPM; SPM-9700, Shimadzu Corporation, Kyoto, Japan). Optical transmittance spectra were measured on the film samples using an optical spectrometer (V-770, JASCO, Tokyo, Japan), where a silica glass substrate was used as the reference. Ellipsometric measurements were conducted for the films deposited on Si(100) substrates, and the XRD and SPM measurements were performed on the silica glass substrates.

3. Results and discussion

3.1. Preparation and characterization of TiO₂ films

Ti(O(C2H5)4)4 solutions of x (H2O/Ti(O(C2H5)4)4 mole ratio) = 1.0 and 8.0 were prepared as coating solutions. At the lower H₂O content of x = 1.0, the amount of HNO₃ was limited to a maximum of y = 0.6 because the addition of a large amount of 69 mass% HNO₃ containing water resulted in an
excessive H$_2$O content. However, the solutions with a higher H$_2$O content of $x = 8.0$ needed the addition of HNO$_3$ over $y = 1.0$ for suppression of the rapid precipitation. Transparent coating solutions of $x = 1.0$ and 8.0 were obtained at $y = 0.6$ and 1.0, respectively (The pH of these solutions checked readily with pH-test paper were below 1.0). The compositions of the coating solutions differed in the x and y values, while we previously found that the HNO$_3$ content in Ti(OC$_3$H$_7$)$_4$ solutions did not strongly affect the crystallinity and microstructure of TiO$_2$ films in the Ti(OC$_3$H$_7$)$_4$ :HNO$_3$ :H$_2$O :C$_2$H$_5$OH system [16].

Precursor gel films were prepared from the coating solutions of $x = 1.0$ ($y = 0.6$) and 8.0 ($y = 1.0$) by dip coating, and then heated at 200–400°C for 10 min–6 h in air. Figure 1 shows the dependence of the film thickness on the heating time for the heat-treated TiO$_2$ films of $x = 1.0$ and 8.0. The film thickness

![Figure 1](image_url)

*Figure 1.* Dependence of thickness on the heating time for the TiO$_2$ films prepared at $x = 1.0$ and 8.0 by heating at 200–400°C.
The crystal phase and the crystallinity of the TiO$_2$ films of $x = 1.0$ and 8.0 heated at 200–400°C were evaluated by XRD. When heated at 200°C, no diffraction peaks were observed in the XRD patterns of the films of $x = 1.0$ and 8.0 (Supplementary Information Figure S1). The diffraction patterns attributed to the anatase phase were detected for the films heated over 300°C. Figure 2 shows the XRD patterns of the films of $x = 1.0$ and 8.0 heated at 300–400°C for 1–6 h. In the case of heating at 300°C, the films of $x = 8.0$ crystallized in anatase within 3 h (Figure 2c), while the films of $x = 1.0$ needed a longer heating time (over 6 h) for generation of the anatase phase (Figure 2a). However, for the films heated at 400°C, the anatase phase appeared by heating for 1 h irrespective of the H$_2$O content (Figure 2b,d). These results suggest that the greater H$_2$O content might slightly accelerate the crystallization in anatase at low temperatures below 300°C. For a quantitative discussion of the nucleation and crystal growth in the heat-treated films, the degree of crystallization and the crystal size of the anatase were calculated from the peak area and the full-width at half-maximum of the XRD patterns, respectively. The peak area and the crystallite size of the anatase calculated with Scherrer’s formula [25–28] are shown in Figure 3, where the values were calculated from the (101) diffraction peaks of the anatase in Figure 2. The peak area (i.e. the degree of crystallization) (Figure 3a) and the crystallite size (Figure 3b) increased with an increase in heating time and temperature, while the variation in $x$ provided no clear difference in the degree of crystallization or crystallite size of the resultant films.

The valence state of titanium atoms in the TiO$_2$ films was evaluated by XPS analysis. The XPS spectra of the films of $x = 1.0$ and 8.0 heated at 400°C for 1 and 6 h are shown in Supplementary Information Figures S2. The valence state of Ti$^{4+}$ species didn’t change irrespective of the H$_2$O and HNO$_3$ contents and the heating time. Moreover, the peaks attributed to N and C atoms were not detected for all the films.

The microstructure of the heat-treated TiO$_2$ films of $x = 1.0$ and 8.0 was measured using an SPM. The SPM images obtained for the films of $x = 1.0$ and 8.0 heated at 400°C for 6 h are shown in Figure 4. The microstructure of the films changed depending on the H$_2$O content, even though the degree of crystallization and the crystallite size were almost unchanged (Figure 3). The film of $x = 8.0$ was found to consist of densely packed fine grains of ca. 20 nm in size (Figure 4b), where the grain size agreed well with the crystallite size calculated from the XRD patterns by Scherrer’s formula (ca. 25 nm). However, inhomogeneous grains 10–150 nm in size, larger than the crystallite size (ca. 25 nm), were observed on the surface of the

![Figure 2](image-url). XRD patterns of the TiO$_2$ films prepared at $x = 1.0$ (a–b) and 8.0 (c–d) by heating at 300 (a, c) and 400 (b, d) °C for 1–6 h.
film of $x = 1.0$ (Figure 4a). In the present case, the TiO$_2$ films were heated at low temperature below 400°C, and thus the crystallinity was relatively low. Therefore, the films of $x = 1.0$ might contain residual amorphous species, resulting in the formation of large secondary particles containing amorphous and small crystallites.

The formation of the dense surface structure with an increase in H$_2$O content could be caused by the activation of hydrolysis of Ti(OC$_3$H$_7$)$_4$ in the coating solutions. The higher H$_2$O content of $x = 8.0$ could activate the generation of TiO$_2$ nuclei in the coating solutions through the faster hydrolysis of Ti(OC$_3$H$_7$)$_4$, which provided the precursor gel films containing a large amount of small crystallites, thus resulting in dense films consisting of fine grains after the heat treatment (Figure 4b). However, much unreacted titanium alkoxides are thought to remain in the precursor gel films of $x = 1.0$, which could

![Figure 3](image-url)  
**Figure 3.** Dependence of peak area (a) and crystallite size (b) on the heating time for the TiO$_2$ films prepared at $x = 1.0$ and 8.0 by heating at 300 and 400°C.
induce inhomogeneous nucleation and crystal growth during the heating and leading to the rough surface consisting of inhomogeneous grains (Figure 4a).

Moreover, in this work, the H$_2$O content did not clearly affect the degree of crystallization or crystal-lute size of the resultant anatase films (Figure 3). The effect of water on the crystallization behavior of TiO$_2$ materials has been widely discussed by many researchers. For example, Yanagisawa et al. reported that the hydrogen bonding by water molecules between the surface OH groups of TiO$_6$ octahedra makes the intermediate structures suitable for the transformation into the face-sharing anatase structure [22]. We also previously studied the crystallization and densification behavior of TiO$_2$ films during heating at 800°C, where the nucleation and growth of anatase were accelerated by the addition of a large amount of water [16]. However, in the present case of heating below 400°C, the difference in the peak area (Figure 3a) and the peak width (Figure 3b) of the XRD patterns (i.e. the degree of crystallization and the crystal size) was not clearly observed for the films of $x = 1.0$ and 8.0. The nucleation and crystal growth of the anatase phase at such low temperatures are deduced to be very slow regardless of the amount of water because of the low driving force for ion diffusion, resulting in no difference in the XRD patterns. However, crystallization of the films of $x = 8.0$ during heating at 300°C occurred slightly faster than did the $x = 1.0$ system (Figure 2). Thus, the large amount of water might slightly assist the crystallization of sol–gel-derived TiO$_2$ films even at relatively low temperatures.

### 3.2. Optical properties of TiO$_2$ films

The optical transmittance of the TiO$_2$ films of $x = 1.0$ and 8.0 heated at 400°C for 1 and 6 h was evaluated with an optical spectrometer. The UV-vis transmittance spectra of the TiO$_2$ films are shown in Figure 5. All the films showed high transmittance at the wavelength over 400 nm. Interference fringes were observed for all the films, which could be attributed to the homogeneous coating layer on the substrates [29]. The films of $x = 8.0$ heated for 6 h exhibited lower transmittance at the wavelengths between 350–500 nm than those of $x = 1.0$. As observed in SPM image (Figure 4b), the film of $x = 8.0$ consisted of densely packed fine grains of ca. 20 nm in size. The porous structure consisting of nanoparticles could enhance the scattering of incident light, resulting in the low transmittance [29–31].

The refractive index of the TiO$_2$ films of $x = 1.0$ and 8.0 heated at 200–400°C for 10 min–6 h were measured by spectroscopic ellipsometry, and the anatase films prepared by heating at 800°C were also evaluated for comparison (the thickness, XRD patterns, peak area, and crystallite size of the films heated at 800°C are shown in Supplementary Information Figure S3 and Table S1). Figure 6 shows the dependence of the refractive index on the heating time for the heat-treated TiO$_2$ films, where the refractive index values at a wavelength of 632.8 nm were taken. The refractive index increased with an increase in heating time and temperature for the films of $x = 1.0$ and 8.0, which indicates that the higher crystallinity and the higher density of the TiO$_2$ films contributed to a higher refractive index. Moreover, the films of $x = 8.0$ exhibited a higher refractive index than those of $x = 1.0$ (Figure 6b), which could be attributed to the dense microstructure (i.e. low porosity) provided by the addition of a large amount of water (Figure 4b). More specifically, the films of $x = 8.0$ heated at 300°C for 6 h and 400°C for 10 min–6 h exhibited an even higher refractive index than those of $x = 1.0$ heated at 800°C.
4. Conclusions

TiO$_2$ films were prepared from Ti(OC$_3$H$_7$I)$_4$ solutions by a so-gel technique, and the effect of water on the crystallization and densification by heating at below 400°C was quantitively discussed. The higher H$_2$O content in the coating solutions slightly accelerated the crystallization of TiO$_2$ during heating at 300°C, while the amount of water did not provide any significant difference in the degree of crystallization or the crystallite size of the resultant anatase films. The increase in the H$_2$O content led to the formation of a dense surface structure consisting of fine grains, which could be obtained through the fast hydrolysis of Ti(OC$_3$H$_7$I)$_4$ in the precursor solutions. The
crystallization and densification assisted by water resulted in a higher refractive index of 2.22–2.25 for the films heated at 300–400°C, which suggests that water-assisted crystallization and densification is an effective route for synthesizing thin film materials with a high refractive index at relatively low temperature.

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Disclosure statement

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