Effects of Addition of Poly(ethylene glycol) on the Formation of Anatase Nanocrystals in SiO_2-TiO_2 Gel Films with Hot Water Treatment

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Effects of the addition of poly(ethylene glycol) (PEG) in SiO_2-TiO_2 gel films on the formation of anatase nanocrystals with hot water treatment were investigated. Anatase nanocrystals were formed in the whole SiO_2-TiO_2 gel films with the addition of PEG by the treatment, whereas in the films without PEG the nanocrystals were formed mainly on the surface of the films. PEG in the SiO_2-TiO_2 films was completely leached out with the hot water treatment in about 1 min. The pores produced by the leaching of PEG probably allow anatase nanocrystals to be formed inside the films. Hydrolysis of Si−O−Ti bonds was presumed to play an important role in the nucleation of anatase nanocrystals in the hot water treatment.

Introduction

Anatase-type titania exhibits high photocatalytic activity and thus has recently attracted a great deal of attention in the field of photocatalysts for decomposition of environmental pollutants such as halogenated organic compounds[1] and for antifouling and antibacterial applications.[2,3] Anatase nanocrystals show higher photocatalytic activities than the bulk crystals because the nanocrystals facilitate the diffusion of excited electrons and holes toward the surface before their recombination.[4] In addition, the anatase nanocrystals must be highly dispersed in the host matrix without aggregation to enhance the activity.[5]

The sol−gel method is one of the suitable techniques for preparing titania and titania-containing multicomponent thin films of which the chemical composition, crystallinity, and texture are precisely controlled.[6−10] The films prepared by the method are usually amorphous before heat treatment, and heat treatment at high temperatures is generally required for crystallization and densification of the films.[10,11] Substrates with poor heat resistance like organic polymers have difficulty in withstanding such a high-temperature process, and therefore lowering the temperatures for crystallization and densification is demanded.

We have recently reported that transparent and porous anatase nanocrystals-dispersed films were prepared by treating SiO_2-TiO_2 gel films containing poly(ethylene glycol) (PEG) with hot water.[12,13] The process temperature is lower than 100 °C under atmospheric pressure. This mild process allows us to form anatase nanocrystals-dispersed films even on the organic polymer substrates.

In this paper, we have compared the changes in microstructure, morphology, and composition of the films with hot water treatment for the SiO_2-TiO_2 gel films obtained with the addition of PEG and without PEG to see the effects of addition of PEG on the formation of anatase nanocrystals in these films.

Experimental Section

$83.5SiO_2 \cdot 16.5TiO_2$ (mol %) coating films were prepared from silicon tetraethoxide and titanium tetra-*n*-butoxide. The preparation procedure of the SiO_2-TiO_2 coating films was essentially the same as that described in our previous papers.[12,13] Silicon tetraethoxide in ethanol was hydrolyzed with water containing 3.6 wt % HCl at room temperature for 30 min;

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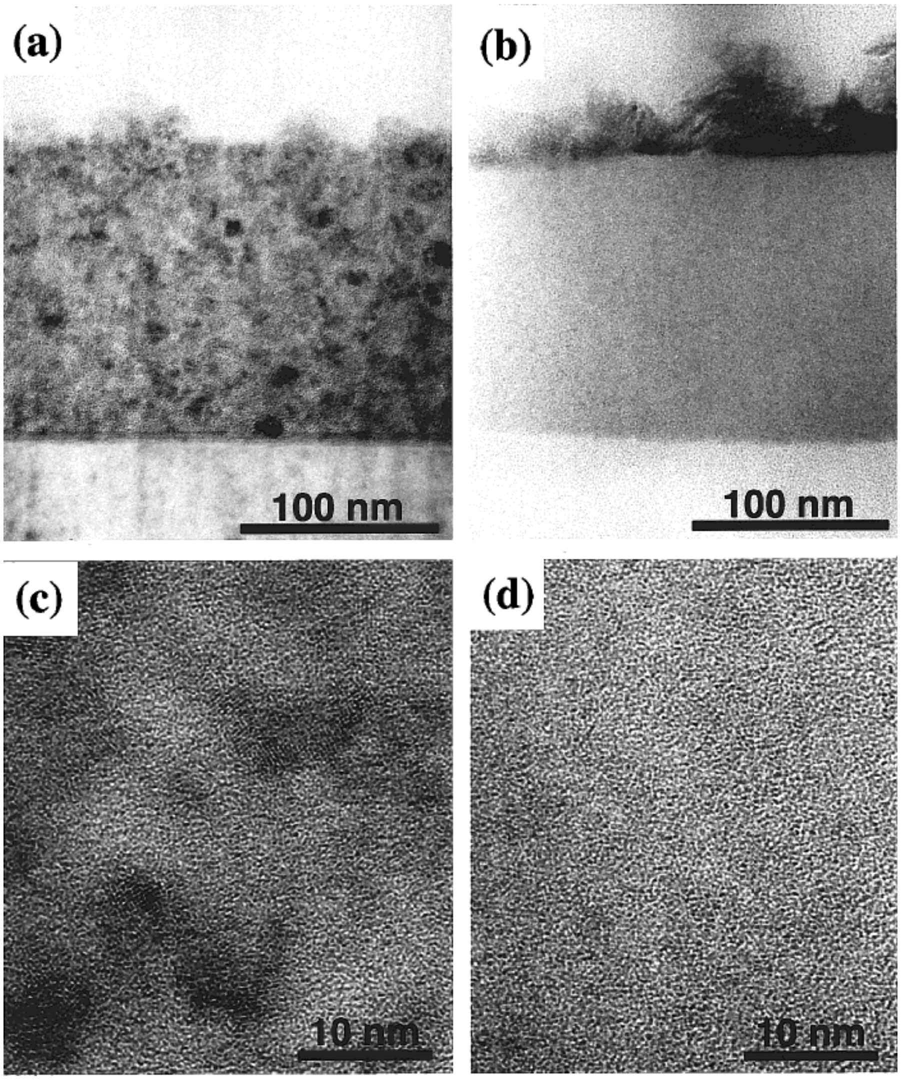

Figure 1. Cross-sectional bright field TEM images of the SiO_2-TiO_2 films obtained (a) with and (b) without PEG after hot water treatment at 97 °C for 60 min. (c) and (d) are the magnified high-resolution images of the selected area inside the films in (a) and (b), respectively.

the mole ratios of ethanol and water to silicon tetraethoxide were 5 and 4, respectively. The hydrolyzed solution was then mixed with titanium tetra-*n*-butoxide diluted with ethanol (the mole ratio of ethanol to titanium tetra-*n*-butoxide was 20) and stirred continuously for 30 min. In the preparation of the films with PEG, PEG with an average molecular weight of 600 was added to the solution and the resultant solution was used for coating. The weight ratio of PEG to SiO_2-TiO_2 oxides was unity. The solution with the same composition without PEG was also prepared for comparison.

The coating was carried out by dipping−withdrawing of a substrate in the atmosphere of about 20% relative humidity at room temperature. The substrates coated with the films were dried at 90 °C for 60 min in air using an oven and then immersed into boiling water for various periods. The changes in texture of the coating films during the hot water treatment were examined using a field-emission-type transmission electron microscope (TEM) (Model HF-2000, Hitachi, Tokyo, Japan) and a field-emission-type scanning electron microscope (FE-SEM) (Model S-4500, Hitachi, Tokyo, Japan). The structure and composition of the films were evaluated using a Fourier transformed infrared (FT-IR) spectrophotometer (Model 1600, Perkin-Elmer, Norwalk, CT) and an energy-dispersive X-ray (EDX) spectrophotometer (Model JED-2001, JEOL) equipped with an SEM (Model JSM-5300, JEOL, Tokyo, Japan). Silicon wafers were mainly used as the substrates to obtain TEM images, FE-SEM images, and FT-IR spectra. Pt−Pd coatings ∼5-nm thick were sputtered on the samples for FE-SEM observation. Aluminum foils were used as the substrates to measure EDX spectra. The thickness of the coating films was measured using a surface profilometer (Model SE-30C, Kosaka Laboratory, Tokyo, Japan). The refractive index of the coating films was determined from the reflectance wavy patterns due to interference between the films and silica glass substrates using a UV spectrophotometer (V-560, JASCO, Tokyo, Japan).

Results and Discussion

Cross-sectional bright field TEM images of the SiO_2-TiO_2 films with the addition of PEG and without PEG after hot water treatment at 97 °C for 60 min are respectively shown in Figure 1, parts (a) and (b). Parts (c) and (d) of Figure 1 are the magnified high-resolution images of a selected area inside the films in parts (a) and (b), respectively. Nanocrystals are observed not only on the surface of the film but also inside the film in Figure 1a. The size of nanocrystals observed inside the film is 5−10 nm in diameter (Figure 1c). Lattice fringes are seen in the nanocrystals formed inside the film. The spacing of the lattice fringe is 0.35 nm, corresponding to the *d*-value of (101) in anatase titania. The nanocrystals were also identified as anatase from the corresponding selected area electron diffraction pattern. On

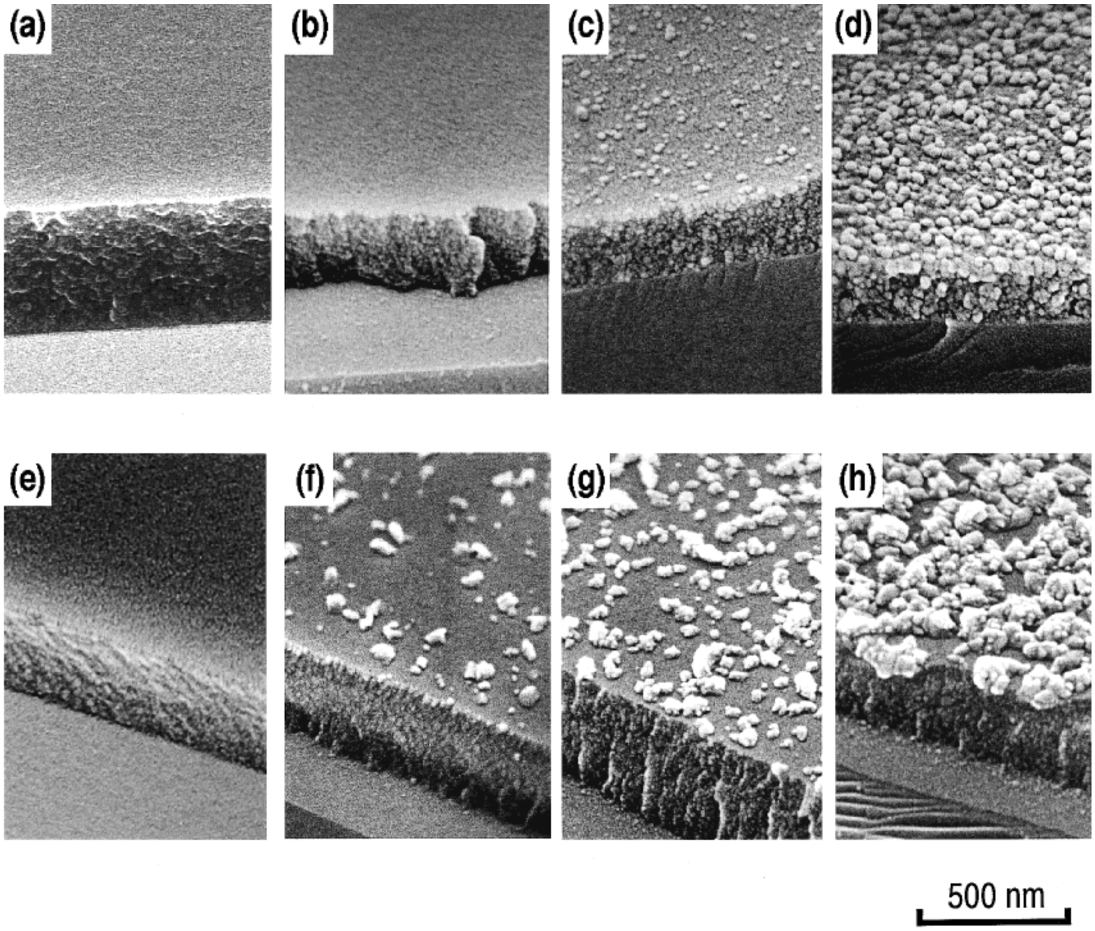

Figure 2. SEM images of the films obtained with PEG addition after hot water treatment for (a) 0, (b) 1, (c) 10, and (d) 60 min. Those of the films obtained without PEG after hot water treatment for (e) 0, (f) 5, (g) 20, and (h) 60 min.

the other hand, in the films without PEG, nanocrystals, which were also identified as anatase, are observed only on the surface of the film in Figure 1b; the size of the nanocrystals is larger in Figure 1b than in Figure 1a. The nanocrystals are not observed inside the film as shown in Figure 1d. No anatase nanocrystals were observed in the SiO_2-TiO_2 films obtained with or without PEG before the hot water treatment. It is thus concluded that the anatase nanocrystals were formed during the hot water treatment and the addition of PEG is necessary to obtain the films with highly dispersed anatase nanocrystals.

The changes in morphology at the surface and cross section of the SiO_2-TiO_2 films with and without PEG during the hot water treatment are compared in Figure 2: parts (a)–(d) of Figure 2 show the SEM images of the films obtained with the PEG addition before the treatment and after the treatment for 1, 10, and 60 min, respectively. Those of the films obtained without PEG before the treatment and after the treatment for 5, 20, and 60 min are respectively shown in parts (e)–(h) of Figure 2. The surface of the film with the PEG addition before the treatment is smooth (Figure 2a). After treatment for 1 min, the film remains smooth, and no precipitates are observed on the film (Figure 2b). The particles less than 40 nm in diameter, which were identified as anatase by TEM, are observed on the surface of the film after the treatment for 10 min (Figure 2c). The size and number of the anatase particles on the surface of the film increase with increasing the treatment time. A number of roundish anatase particles of ca. 50 nm in diameter are observed after treatment for 60 min (Figure 2d). In addition, the cross section of the film becomes rough, probably because of the formation of anatase precipitates inside the film as shown in parts (a) and (c) in Figure 1. The surface of the film without PEG before the treatment (Figure 2e) as well as that of the film with PEG (Figure 2a) is smooth. The anatase precipitates of 10–50 nm in diameter are observed on the surface of the film after the treatment for 5 min (Figure 2f). Similar to the film with PEG, the number of anatase particles on the surface of the film increases with increasing the treatment time, and these particles grow and aggregate to form larger particles as seen in Figure 2g. The anatase particles on the surface of the film without PEG treated for 60 min are rocklike and their diameters are 50–200 nm (Figure 2h): these particles are larger than those precipitated by treating the PEG-containing films with hot water. The cross section of the film without PEG (Figure 2h) is smoother than that of the film with PEG (Figure 2d) after the treatment. These results correspond to the fact that anatase nanocrystals are not formed inside the films without PEG as shown in parts (b) and (d) of Figure 1.

IR absorption spectra of SiO_2-TiO_2 films, which were obtained with and without PEG and treated with hot water for several periods, are shown in parts (a) and (b) of Figure 3, respectively. The absorption band at 2800 cm^{-1} due to C–H bonds in PEG disappears after

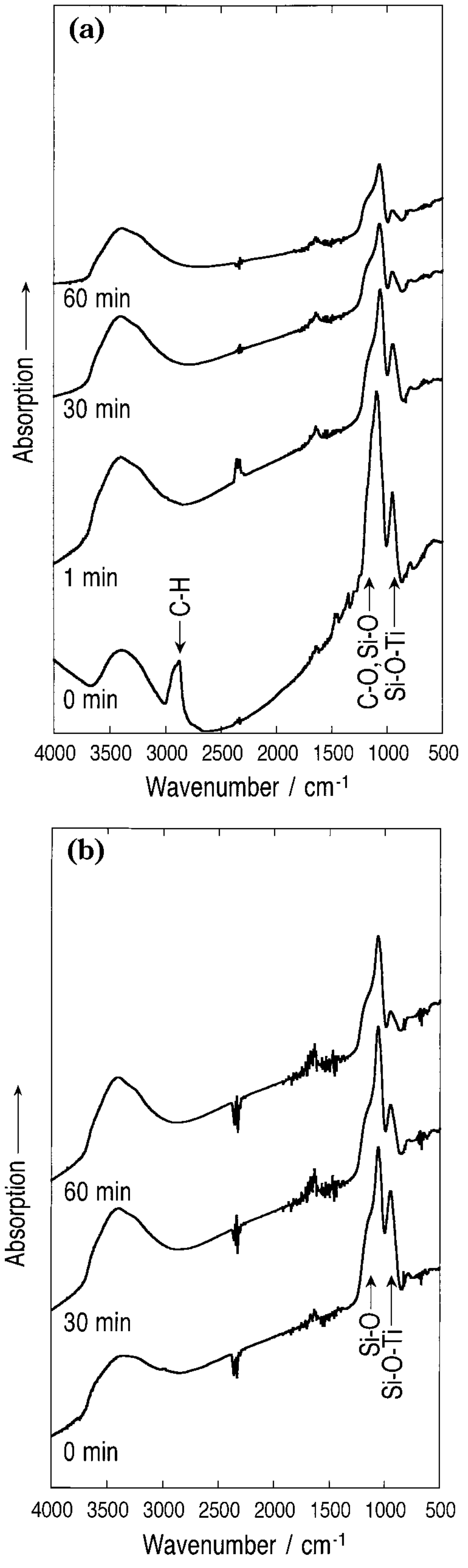

Figure 3. IR absorption spectra of SiO_2–TiO_2 films obtained (a) with and (b) without PEG during hot water treatment for various periods of time.

treatment for 1 min (Figure 3a), indicating that PEG is completely leached out with hot water. The strongest absorption band in the spectra of the films that were obtained with the PEG addition and not subjected to the hot water treatment is observed at around 1100 cm^{-1}, which is assigned to the overlapping of the stretching modes of Si–O bonds in SiO_2–TiO_2 and C–O bonds in PEG. The intensity of the band at around 1100 cm^{-1} decreases largely with the treatment for 1 min, which should be caused by both the leaching of PEG and dissolution of the films into hot water. After 1 min, the intensity of this band continuously decreases due to dissolution of the films. The intensity of an absorption band at 950 cm^{-1} mainly due to Si–O–Ti bonds[14,15] decreases more appreciably with the treatment. This result suggests that the Si–O–Ti bonds are readily hydrolyzed with hot water. On the other hand, the intensity of the absorption band due to Si–O bonds in the films without PEG slightly decreases with increasing treatment time (Figure 3b). In the films without PEG, the dissolution of the films gradually occurs with increasing treatment time. The intensity of the absorption band due to Si–O–Ti bonds in the films without PEG also decreases with the treatment.

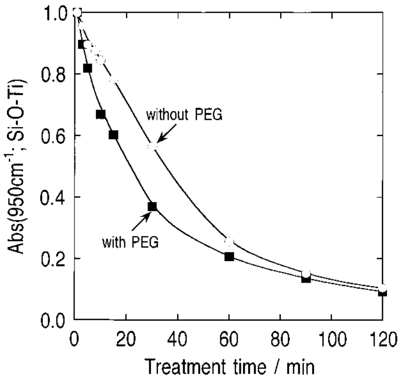

Figure 4. Changes in the relative intensity of the IR absorption band at 950 cm^{-1} in the SiO_2–TiO_2 films with and without PEG as a function of the hot water treatment time.

Figure 4 shows the changes in intensity of the IR absorption band at 950 cm^{-1} due to Si–O–Ti bonds in the SiO_2–TiO_2 films with and without PEG as a function of hot water treatment time. In 1 min of the treatment for the films with PEG, PEG was completely leached out and the films were dissolved as shown in Figure 3a. The intensity of the band at each hot water treatment time was normalized with that of the band of the films that were subjected to the treatment for 1 min. The relative intensities of the band in both films with and without PEG monotonically decrease. The monotonical decrease in the relative intensity of the bands in the films with and without PEG can mainly be ascribed to the hydrolysis of Si–O–Ti bonds. The very low values of the intensity of the band after treatment for 120 min mean that almost all the Si–O–Ti bonds in the entire film are hydrolyzed with hot water regardless of the addition of PEG into the films.

It is important to report that anatase nanocrystals were not formed in the pure TiO_2 gel films with the same hot water treatment. Thus, the formation of anatase nanocrystals with hot water treatment is concluded to be a unique phenomenon in the present SiO_2–TiO_2 system. It is presumed that the hydrolysis or dissociation of Si–O–Ti bonds in the SiO_2–TiO_2 gel

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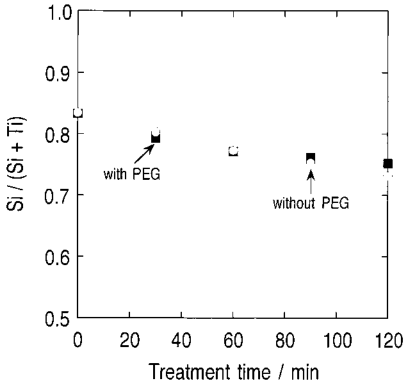

Figure 5. Changes of Si/(Si + Ti) atomic ratio of the SiO_2-TiO_2 films with and without PEG by hot water treatment.

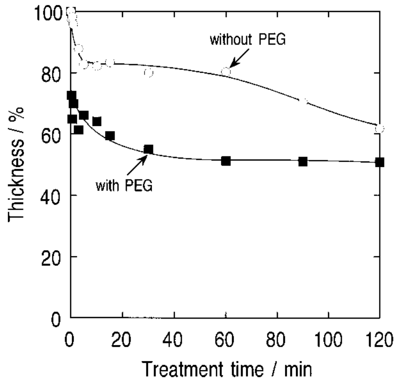

Figure 6. Changes in thickness of the SiO_2-TiO_2 films with and without PEG during hot water treatment.

films plays an important role in the nucleation of anatase nanocrystals.

The refractive index of the SiO_2-TiO_2 films with PEG was 1.47−1.50 after the hot water treatment for 1 min, whereas that of the films without PEG before the treatment was ca. 1.52. Porosity and refracive indexes of porous films can be related by

$$(n_c^2 - 1)/(n^2 - 1) = 1 - P/100 \qquad (1)$$

where n_c and n are the refractive indexes of porous film without adsorbed water and of the nonporous bulk, respectively, and P is the percent porosity.[16] The value (=1.60) of the refractive index for nonporous $83.5SiO_2 \cdot 16.5TiO_2$ bulk glass was estimated by assuming the additivity in the refractive index between SiO_2 (=1.46) and TiO_2 (=2.30). Porosity of the SiO_2-TiO_2 films with PEG after hot water treatment for 1 min was calculated from eq 1 to be 20−26%, whereas that of the films without PEG before the treatment was ca. 16%. The calculated porosity of the films should be lower than the actual porosity because the films contain adsorbed water. The porosity of the SiO_2-TiO_2 films with PEG after hot water treatment for 1 min is higher than that of the films without PEG before the treatment, indicating that the resultant films after the leaching of PEG are more porous than the films without PEG. Dissociated TiO_2 species with hot water treatment form anatase nanocrystals inside the films with PEG addition bacause of the porous structure of the films. On the other hand, dissociated TiO_2 species migrate through the films without addition of PEG to precipitate anatase nanocrystals only on the surface of the films since the films are not so porous as to allow the TiO_2 species to form anatase nanocrystals inside the films.

The changes in the composition of the SiO_2-TiO_2 films with and without PEG during hot water treatment are shown in Figure 5. The atomic ratio of Si/(Si + Ti) in Figure 5 was obtained using EDX. In both films with and without PEG, the Si/(Si + Ti) ratios gradually decrease with the treatment time, indicating that SiO_2, which has a higher solubility than TiO_2,[17,18] was preferentially dissolved with the treatment. The ratios of both films decrease roughly from the initial value 0.84 to 0.74 in 120 min.

Figure 6 shows the changes in thickness, that is, shrinkage, of the SiO_2-TiO_2 coating films with and without the addition of PEG during hot water treatment. The thickness of the films with PEG before the treatment was about 320 nm, which decreases rapidly to 70% in 1 min and then gradually to 50% in 120 min by the treatment. The drastic decrease of the thickness in 1 min of the treatment corresponds to the leaching of PEG from the gel films and the partial dissolution of the gel films. It has been reported that the porosity of sol−gel-derived silica films decreases upon exposure to high temperature and high humidity, leading to densification of the films.[19,20] The later gradual decrease of the thickness is probably due to partial dissolution of the films as shown in Figure 3a and densification of the films. On the other hand, the thickness of the films obtained without PEG, which was about 230 nm before the treatment, decreases to 80% in the first 10 min during the treatment and then fluctuates to become 60% in 120 min. The initial rapid decrease should be due not to the partial dissolution of the gel films but to the densification of the films because the intensity of the IR absorption band due to Si−O bonds in the films without PEG was almost constant in this period, as seen in Figure 3b. The fluctuation in the thickness of the films in successive treatment after 10 min probably reflects the growth of anatase particles on the surface of the films and partial dissolution of the films during the treatment as shown in Figure 3b.

Conclusions

We have investigated the effects of the addition of PEG in SiO_2-TiO_2 gel films on the formation of the anatase nanocrystals with hot water treatment. The formation of anatase nanocrystals in the films with and without PEG gradually proceeded with increasing treatment time. Hydrolysis or dissociation of Si−O−Ti bonds in the SiO_2-TiO_2 films obtained both with and without PEG proceeded with hot water treatment. The anatase nanocrystals were formed in the whole films containing PEG, whereas they were formed only on the surface of

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the films without PEG. PEG in the films was readily leached out with hot water and the resultant films became porous. The pores produced after leaching of PEG must allow anatase nanocrystals to be formed inside the resultant films. On the other hand, the pore volume of the films without PEG may be too small to form anatase nanocrystals. Dissociated TiO_2 species with hot water treatment in the films without PEG should migrate from the inside to the surface of the films to form anatase precipitates on the surface of the films.

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