Titanium oxide thin film preparation with sol coatings of plate and spindle-shaped nanoparticles for control of optical transmittance

Chun Ming WEN, Naofumi UEKAWA,† Khakkhanang KHAMFOO† and Takashi KOJIMA

Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan
†Faculty of Science, Khon Kaen University, 123 Moo 16 Mittapap Rd., Nai-Muang, Muang District, Khon Kaen, Thailand

A layered titanate sol was prepared at room temperature (298 K) using dialysis of a mixed solution of ethylene glycol solution of TiCl4, ammonium carbonate aqueous solution, and hydrogen peroxide. A sol with dispersion of plate-shaped layered titanate nanoparticles was obtained. A stable sol with dispersion of spindle-shaped anatase TiO2 nanoparticles was obtained by heating the sol with dispersion of layered titanate at 368 K for 24 h in a closed vessel. The optical transmittance spectrum of the TiO2 thin film obtained by coating the sol with dispersion of anatase nanoparticles and firing at 773 K for 1 h showed no interference of an incident light beam into the TiO2 thin film. Optical characteristics on interference originated from pores among TiO2 primary nanoparticles in the thin film, which caused incoherent scattering of incident light into the thin film. When the sols containing both of the plate-shaped layered titanate nanoparticles and the spindle-shaped anatase nanoparticles were used as the coating solution, the interparticle pore volume was controlled by the volume ratio of the anatase sol in the coating solution. The effects of interference on the optical transmittance spectra of the thin films depended on the interparticle pore volume.

Key-words: Titanium oxide, Anatase, Thin film, Optical transmittance, Pore, Interference

1. Introduction

Titanium oxide (TiO2) has potential applications. For example, anatase TiO2 can be applied as photocatalysts, coating materials for controlling UV-shielding properties, and dye-sensitized solar cells.1-3) Valence-controlled anatase TiO2 such as Nb5+ doping has also attracted interest for use as an optically transparent electrical conductive material.4,5) To use these characteristics, it is important to develop methods for obtaining anatase TiO2 thin films with transparency for visible light. TiO2 has a large refractive index, which causes interference among the reflected lights on a film surface and the interface between a film and a substrate.6) The interferences lead to coloration of TiO2 thin films, which inhibits the applicability of TiO2 thin films. Accordingly, it is important issue to develop the TiO2 thin films with less dependence of optical transmittance on wavelength in visible light region due to interference. The optical transmittance of the TiO2 thin films depends on aggregated structures of primary particles in the thin films. Particularly it is necessary that the primary particles in the TiO2 thin films should be smaller than the wavelength of visible light to inhibit the effects of light scattering on the grain boundary and particle surface. The TiO2 thin films with controlled optical transparency are important devices for photocatalysts as environmental purification material.

Various TiO2 thin film preparation methods have been reported. Particularly, solution processes are environmentally friendly, prompting many studies of them.7,8) Wang et al. prepared TiO2 thin films with microspheres using chemical bath deposition.9) Arunachalam et al. prepared Zn-doped TiO2 thin films with strong orientation along (101) using spray pyrolysis technique.10) Dinh et al. produced TiO2 anatase thin films with orientation along (101) using a dipping sol–gel method with a Ti alkoxide solution.11) Haimi et al. investigated optical properties of anatase TiO2 thin films obtained using a non-aqueous sol–gel dip-coating method.12) These simple solution processes are widely applicable for thin film preparation.

This research examines not only the control of optical transparency but also the advanced control of optical characteristics such as inhibition of interference coloring of the TiO2 thin films using a simple and environmental friendly process with titanium oxide sols. To control the optical characteristics of the thin films, controlling the aggregated structure of the primary particles in the thin films is necessary.13,14) Stable sols with dispersion of shape-controlled and size-controlled titanium compound nanoparticles are useful as coating solutions. Drying the sols and firing on the glass substrate enables us to obtain TiO2 thin films. Their interparticle pores and orientation of crystals depend on the size and shape of particles in the thin films. Furthermore, these TiO2 nanoparticles and sols are obtainable using solution processing with a low environmental load.

In this study, preparation of the TiO2 thin films with controlled optical transmittance and no interference was examined by regulation of the porosity and aggregated structure in the TiO2 thin films. The regulation was examined using sols including different types of shapes of the titanium oxide nanoparticles as a coating solution. Amount of interparticle pores in the obtained thin films were tried to be controlled by the volume fraction of spindle-shaped nanoparticles and plate-shaped nanoparticles. These shape controlled titanium oxide nanoparticles and their stable sols were prepared using solution process. The TiO2 thin films...
were prepared by drying and firing the sols on a glass substrate. The effect of the porosity on the optical transparency of the thin films was discussed.

2. Experiments

2.1 Preparation of layered titanate sol and heat treatment of the sols

Sols of layered titanate particles were prepared as follows: 3.85 g of titanium chloride (III) (TiCl₃) aqueous solution (20 wt%, Ti³⁺ 0.005 mol) was dissolved in 10 mL of ethylene glycol. The 2.4 g (0.025 mol) of ammonium carbonate (NH₄)₂CO₃ was dissolved in 10 mL of H₂O. This aqueous solution was mixed with an ethylene glycol solution of TiCl₃. After the formation of a titanium hydroxide precipitate, H₂O was added to adjust the solution volume to 50 mL. The 5.67 g of 30 wt% hydrogen peroxide (H₂O₂) aqueous solution was added to the solution. The hydroxide precipitate was peptized spontaneously, producing a clear yellow solution. The solution was packed in a cellulose tube to be dialyzed in H₂O. After dialysis, yellow clear sols were obtained. The whole preparation process was conducted at room temperature (298 K). Furthermore, the obtained sols were packed in a closed vessel and were heated at 368 K for 24 h. The heat treatments of the sols at 348 and 328 K were also examined. The obtained sols were dried at 328 K for 24 h to obtain powder samples. All chemicals used in this preparation were of reagent grade (Wako Pure Chemical Industries Ltd.).

2.2 Thin film preparation by coating sols onto a glass substrate

First, 10 mL of the obtained sol and the 10 mL of H₂O were poured into a glass dish of 10.0 cm diameter. Then, ozone-cleaned alkali-free square glass plate (50 mm × 50 mm × 1 mm) was put on the glass dish, which was then heated at 328 K for 12 h to dry. Finally, the thin film was obtained on the alkali-free glass plate. The obtained thin films were fired under air atmosphere at 773 K for 1 h to obtain TiO₂ thin films. To increase the film thickness, the procedures used for drying sols on the substrate and firing the films were repeated.

2.3 Characterization

Structures of the obtained particles and thin films were characterized using X-ray diffraction (XRD, Cu Kα, 40 kV, 15 mA, Mini Flex; Rigaku Corp.) with a Ni filter. The particle shape was observed using field emission scanning electron microscopy (FE-SEM, JSM-6330; JEOL Ltd.) after Os coating. Furthermore, the observation of the particle shape was carried out using transmission electron microscopy (TEM, H-7650 Hitachi High Technologies Corp.). Raman spectra of the powders obtained by drying the sols were measured using NRS-2100; Jasco Ltd. The ultraviolet–visible (UV–VIS) spectra of the sols and the thin films were measured (UV2000; Shimadzu Corp.) with wavelengths of 300–800 nm. The N₂ adsorption isotherms of the obtained powders were measured at 77 K using the volumetric method (BELSORP-max; BEL Japan Inc.) after pretreatment at 383 K in 1 mPa for 1 h.

3. Results and discussion

3.1 Characterization of obtained sols

Figures 1(a)–1(d) show XRD patterns of the powders obtained by drying the sols. Figure 1(a) shows the XRD pattern of the powder obtained by drying the sol without heat treatment. The diffraction peak around 2θ = 8.9° corresponds to the distance of the interlayer of a layered titanate structure. Hereinafter, the sol with dispersion of layered titanate particles was designated as “layered titanate sol”. When the heating temperature of the sol was 348 K, the XRD pattern of the particles as presented in Fig. 1(b) can also be assigned to the layered titanate. When the heating temperature of the sol was 358 K, the XRD pattern of the particles as presented in Fig. 1(c) can be assigned to the layered titanate. When the heating temperature was 368 K, the XRD peaks in Fig. 1(d) can be assigned to anatase TiO₂. Accordingly, the heat treatment of the sol with dispersion of the layered titanate particles (the layered titanate sol) at 368 K formed anatase TiO₂. The sol obtained by heating the layered titanate sol at 368 K for 24 h was designated as “anatase sol”.

Transformation from layered titanate to anatase was rapidly occurred within the temperature range from 358 to 368 K. In order to examine the reason, Raman spectra of the powders obtained by drying the sols were measured as shown in Fig. 2. The Raman peaks in the spectra of Figs. 2(a) and 2(b) whose Raman shift wavenumbers around 280, 500, and 680 cm⁻¹, can be assigned to the symmetric vibration modes as a well-developed 2D layered structure. Furthermore, the peak around 900 cm⁻¹ can be assigned to the peroxo group. The particles obtained by heating the layered titanate sol at 348 and 358 K had peroxo groups whose origin was H₂O₂. The coordination of peroxo groups to Ti ions inhibited the structural transformation to anatase TiO₂. On the other hand, the particles obtained by heating the layered titanate sol at 368 K, the Raman peak which corresponded to the peroxo group around 900 cm⁻¹ disappeared and the peaks which can be assigned to anatase TiO₂ appeared as shown in Fig. 2(c). Accordingly, the disappearance of the peroxo groups which coordinated to Ti ions enabled to transform the crystal structure from layered titanate to anatase.
obtainable. The sols with dispersion of particle shapes of different types are observable. Drastic change of the particles in the anatase sol. The image of the spindle shaped nanoparticles can be clearly observed. Figure 4(d) showed the TEM image of the spindle shape were obtained as described in Fig. 4(c). The average sizes of the longer axis and the shorter axis were, respectively, 134 and 46 nm. Figure 4(d) showed the TEM image of the particles in the anatase sol. The image of the spindle anatase nanoparticles can be clearly observed. Drastic change of the nanoparticle shape occurred simultaneously with the crystal structure transformation from layered titanate to anatase. Here, the sols with dispersion of particle shapes of different types are obtainable.

**Figure 3** shows UV–VIS transmittance spectra of the obtained sols. The UV–VIS transmittance spectra of the layered titanate sol are presented in Fig. 3(a). The optical transmission at 450 nm was greater than 80%. This high optical transmittance indicated that aggregation of the particles dispersed in the layered titanate sol was slight. In general, aggregation of particles in a sol causes light scattering, which decreases optical transmittance of sols. Furthermore, Ti$^{4+}$ ions have the optical absorption which corresponds to d–d electron transition around 500 nm. On the other hand, Ti$^{3+}$ ions have no 3d electrons and do not show the d–d transition peak.\(^\text{17)}\) Accordingly, the Ti ions in the layered titanate sols are Ti$^{4+}$, which was formed by oxidation of Ti$^{3+}$ by H$_2$O$_2$. Furthermore, the electron-rich ligands such as hydroxyl groups and carboxylate groups coordinate to Ti ions, the ligand-metal charge transfer (LMCT) absorption occurs.\(^\text{18,19)}\) The decrease of the transmittance below 400 nm corresponded to charge transfer absorption between O$^2-$ (2p) and Ti$^{4+}$ (3d). When the heating temperatures of the layered titanate sol were under 358 K, the layered titanate particles in the sols were dispersed stably. Furthermore, when the heating temperature of the layered titanate sol was 368 K, the optical transmittance at 345 nm was 32%, as presented in Fig. 3(d). This result shows that the anatase particles in the sol were also dispersed stably in the sol without precipitation. For large aggregated structures existing in the sols, the transmittance approaches 0%.

The FE–SEM image of the particles in the layered titanate sol is depicted in Fig. 4(a). Nanoparticles with a plate shape were observed. The average particle size was 91 nm. When the layered titanate sols were heated at 358 K for 24 h, the particles in the sol were also nanoparticles with a plate shape having average diameter of 121 nm, as presented in Fig. 4(b). The plate shape corresponds to the layered structure. However, when the heating temperature of the layered titanate sol was 368 K, nanoparticles with spindle shape were obtained as described in Fig. 4(c). The average sizes of the longer axis and the shorter axis were, respectively, 134 and 46 nm. Figure 4(d) showed the TEM image of the particles in the anatase sol. The image of the spindle anatase nanoparticles can be clearly observed. Drastic change of the nanoparticle shape occurred simultaneously with the crystal structure transformation from layered titanate to anatase. Here, the sols with dispersion of particle shapes of different types are obtainable.

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Furthermore, anatase TiO$_2$ (101) is the most thermodynamically stable crystal face.$^{15}$

Figures 5(c) and 5(d) present XRD patterns of the thin films obtained by repeating the coating procedures of the anatase sol. When the number of coating times were 1 and 5, the XRD peaks of (101), (200), and (211) alone appeared. In cases where the anatase sol was used for thin film preparation, the XRD peak intensity not only of (101) but also of (200) was stronger than those of the other XRD peaks, which indicates that the anatase thin film prepared using the anatase sol had the (200) orientation of the crystallites. Nanoparticles in the anatase sol have a spindle shape. Formation of an arrangement of spindle anatase nanoparticles during the drying process in the coating played an important role in formation of the orientation. Furthermore, these simple coating techniques can be utilized for the control of crystallite orientation in the TiO$_2$ thin films.

The optically transparent anatase thin films have important applications for photocatalyst and UV shielding materials. Therefore, optical transmittance of the obtained anatase thin films was examined. Figures 6(a) and 6(b) show transmittance spectra of thin films obtained using the coating procedures with the layered titanate sol. The dependence of the transmittance values on the wavelength indicated a swing curve. Furthermore, when the number of the coating times increased from 1 to 5, the number of local peaks increased. This increase indicates that the increased thin film thickness enhanced interference of the incident light beam into the thin films because of interference among the reflected light on the thin film surface and the interface between a film and a substrate. Figures 6(c) and 6(d) show the optical transmittance spectra of the anatase thin films obtained using the coating procedures with the anatase sol and number of the coating times respectively as 1 and 5. The values of the optical transmittance were more than 90\% for wavelengths of 450–800 nm. Furthermore, the dependence of the transmittance on the wavelength showed no swing curve. The transmittance spectra of the thin films obtained using the layered titanate sol were quite different from those obtained using the anatase sol. Results show that the transmittance spectra of the thin films obtained using the anatase sol were unaffected by interference of the incident light beam. The TiO$_2$ thin films without effect of the interference on the transmittance spectra are required for the application of photocatalyst coatings on glasses. Therefore, it is necessary to investigate the factors to affect the optical transmittance spectra of the TiO$_2$ thin films.

3.3 Relation between optical transmittance of thin films and aggregated TiO$_2$ nanoparticle morphology

The optical transmittance of TiO$_2$ thin films depends on the thickness and aggregated morphology of TiO$_2$ nanoparticles in the thin film. Therefore, the FE–SEM images of the cross sections of the thin films obtained using the layered titanate sol and the anatase sol were observed respectively as shown in Figs. 7(a) and 7(b). The thin films were coated five times. The thin film thicknesses obtained using the layered titanate sol and the anatase sol were, respectively, 210 and 310 nm. Accordingly, the difference of the thickness between these films was not too large to influence the effects of interference on the transmittance spectra. The roughness of the thin film surfaces was different. The thin film obtained using the anatase sol had rougher surface than that obtained using the layered titanate sol. The roughness of the surface cause diffused reflection of light and decrease the optical transmittance of the thin films. As shown in Figs. 6(c) and 6(d), the values of the optical transmittance were more than 90\% for wavelengths of 450–800 nm. Accordingly, the roughness of the surfaces of the thin films did not affect the values of the optical transmittance. The aggregated morphology of the anatase nanoparticles in both anatase thin films indicated some differences.

The dense aggregation of the primary nanoparticles was observed in the FE–SEM image of the thin film obtained with the layered titanate sol in Fig. 7(a). The FE–SEM image of Fig. 7(b) describes loosely aggregated structures of the spindle anatase nanoparticles.

To examine more details related to the aggregated structure of the TiO$_2$ nanoparticles in the thin films, the N$_2$ adsorption isotherms were measured at 77 K. The powders used for measurements were obtained by drying the sols, followed by firing at 773 K for 1 h. Figures 8(a) and 8(b) show the N$_2$ adsorption isotherms of the powders obtained respectively from the layered titanate sol and the anatase sol. The BET specific surface area ($S_{BET}$) of the powders obtained from the layered titanate sol and the anatase sol were, respectively, 28.7 and 110 m$^2$/g. The pore volumes of the particles ($V_{pore}$) were estimated by the adsorbed amount of N$_2$ at $P/P_0 = 0.99$. The values of $V_{pore}$ of the powders obtained from the layered titanate sol and the anatase sol were, respectively, $5.5 \times 10^{-2}$ and $3.6 \times 10^{-1}$ cm$^3$/g. The values of $S_{BET}$ and $V_{pore}$ of the powder obtained from the layered titanate sol were less than those of the powder obtained from the anatase sol. This result demonstrated that the powder obtained from the layered titanate sol had more strongly aggregated morphology of the primary TiO$_2$ nanoparticles than powders obtained from the anatase sol. Accordingly, this densely aggregated morphology in the thin films caused the interference of incident light beam among the reflected light on the thin film surface and the interface between the thin film and the substrate. However, the powders...
The transmittance spectra of the coating solutions. The transmittance spectra of the anatase sol and the layered titanate sol used for coating solutions was at 773 K for 1 h. The volume fractions of the anatase sol in the mixed solutions \((x_{\text{anatase}})\) were (a) 0, (b) 0.1, (c) 0.2, (d) 0.5, and (e) 1.

obtained by drying the anatase sol had pores with average diameter of 25 nm, as estimated using the BJH method. According to the particle size of the spindle anatase nanoparticles, the average pore size corresponded to the interparticle pores. The large \(V_{\text{pore}}\) of the powder obtained from the anatase sol reflects that the powder had numerous interparticle pores with pore diameter too small to decrease the transmittance of visible light. When the incident light passes through the anatase thin film with the interparticle pores, incoherent light scattering occurs at the interface among the interparticle pores and the primary particles so that no effect of the interference on the transmittance spectra was observed in Figs. 6(c) and 6(d).  

To assess the relation between the interparticle pore volume \(V_{\text{pore}}\) and the effect of the interference on the transmittance spectra, the anatase thin films were prepared using the coating solution of mixture between the layered titanate sol and the anatase sol. Hereinafter, the volume fraction of the anatase sol in the coating solution was referred as \(x_{\text{anatase}} = V_{\text{anatase}}/(V_{\text{layered titanate}} + V_{\text{anatase}})\), where \(V_{\text{anatase}}\) and \(V_{\text{layered titanate}}\) are the respective volumes of the anatase sol and the layered titanate sol used for the preparation of the coating solutions. The transmittance spectra of the thin films with five times coating are shown in Fig. 9. When the volume fraction of the anatase sol in the coating solution \(x_{\text{anatase}}\) increased from 0 to 0.2, the effect of the interference on the transmittance spectra decreased as shown in Figs. 9(a)–9(e). However, the maximum and minimum peaks still exist in the transmittance spectra because of the interference. When the value of \(x_{\text{anatase}}\) increased from 0.2 to 1, effects of the interference on the transmittance spectra decreased as shown in Figs. 9(c)–9(e). This change of the transmittance spectra indicated that the aggregated structure of the primary nanoparticles in the thin films increased the number of the sites to cause the incoherent scattering of the incident light beam into the thin films without decrease of the optical transmittance within visible light wavelength region. It is necessary to examine the relation between the \(x_{\text{anatase}}\) value and the aggregated structure in the thin films such as porosity. Although it is difficult to investigate the porosity of the anatase thin films by the \(N_2\) adsorption measurement, correlation was found between the porosity of the powders obtained by drying the sol and firing at 773 K for 1 h and the porosity in the TiO\(_2\) thin films. Figure 10 describes the dependence of the \(S_{\text{BET}}\) and the pore volume \(V_{\text{pore}}\) on the value of \(x_{\text{anatase}}\).

Fig. 8. \(N_2\) adsorption isotherms of the powders obtained by firing the dried sols at 773 K for 1 h. The sols were (a) the layered titanate sol and (b) the anatase sol.

Fig. 9. UV–VIS transmittance spectra of the thin films obtained using a mixture of the layered titanate sol and the anatase sol as coating solutions. The number of coating procedure iterations was 5; the firing condition was at 773 K for 1 h. The volume fractions of the anatase sol in the mixed solutions \((x_{\text{anatase}})\) were (a) 0, (b) 0.1, (c) 0.2, (d) 0.5, and (e) 1.

Fig. 10. Relation between \(S_{\text{BET}}\) and pore volume \(V_{\text{pore}}\) on the value of \(x_{\text{anatase}}\).
Mixing the sols including the nanoparticles with some different types of shapes effectively formed the anatase thin films with the interparticle pores, which can be controlled by the volume fraction $x_{\text{anatase}}$ of the mixed sols. This simple process can be utilized for preparing anatase thin films with no interference and high transparency, which are suitable for photocatalyst films.

4. Conclusion

Layered titanate sols were prepared by peptization of titanium hydroxide obtained by mixing ethylene glycol solution of TiCl$_3$ and ammonium carbonate aq. Dialysis of the peptized solution of titanium hydroxide with a cellulose tube formed a sol with dispersion of layered titanate nanoparticles having plate shape. Furthermore, the stable sol with dispersion of anatase TiO$_2$ nanoparticles is obtainable by heating the layered titanate sol at 368 K for 24 h in a closed vessel. The optical transmittance spectrum of the anatase thin film obtained by coating the anatase sol showed no effect of interference. The characteristics originated from the presence of pores among the nanoparticles. The thin film obtained using the anatase sol had aggregated structure of spindle-shaped anatase nanoparticles with interparticle pores. Furthermore, the number of the interparticle pores can be controlled using the coating solution of the mixture of the layered titanate sol and the anatase sol. The amount of the interparticle pores increased concomitantly with increased $x_{\text{anatase}}$ in the coating solution. The effect of interference on the optical transmittance spectra depended on the amount of the interparticle pores, which cause the incoherent scattering of a incident light beam in the thin films.

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