Effect of Photoirradiation on the Properties of Layered Titanate Thin Films from Transparent Aqueous Titanate Sols

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UV irradiation on films prepared by a spin-coating method using aqueous titanate sols was investigated. The transparent sols used in this study were prepared by a reaction of titanium tetraisopropoxide (TIP) with tetramethylammonium hydroxide (TMAOH) or alkylamines, and consisted of a layered compound. The refractive indices and hardening of the films increased with the irradiation time, indicating that photoirradiation accelerated densification of the films. It was found that these phenomena were caused by the photocatalytic decomposition of alkylammonium ions located between the titanate sheets to contract the interlayer distance. Interestingly, when the film prepared from the TIP–TMAOH sol containing 30 mol% of sucrose to Ti was irradiated through a patterning mask and subsequently heated in air at 500 °C, the irradiated part of the film selectively turned dark brown due to residual carbon. It was thought that sucrose molecules were confined within the host titanate layers densificated by UV irradiation and that the oxidation of the sucrose by oxygen in air was difficult under heating because the densificated titanates might suppress the diffusion of oxygen.

On the other hand, such coloring of the films by sucrose was not found for films prepared from an aqueous suspension of crystalline TiO_2 (anatase), an aqueous solution of TIP–lactic acid (LA)–NH_3, and alcoholic sols such as the TIP–diethanolamine (DEA) system.

Recently, the low-cost, low-energy fabrication of functional materials has been attracting attention from industrial and environmental points of view. A sol–gel technique, which is one of the promising solution processes, is widely used to prepare oxide films and oxide gel films.[1] Using water as a solvent is the most favorable, but many transition metals with higher formal oxidation states are readily hydrolyzed to give insoluble metallic acids. Therefore, chelate compounds are often used to form a stable aqueous solution of them.

Photoirradiation to the gel films consisting of chelate compounds makes it possible to decompose organic chelates to promote densification of the gel films. Light corresponding to ligand-to-metal charge transfer (LMCT) is especially effective because metal-chelate bonds would be weakened. As a result, the irradiated part of films became insoluble into the solvent. Utilizing this difference in solubility, fine patterning of the oxide films has been prepared.[2–5]

We have previously reported that halogen-free, transparent, aqueous colloidal metallate solutions were prepared by a reaction of metal alkoxide (Ti, V, Nb, Ta, Al, and Si) with tetramethylammonium hydroxide (TMAOH) or bulky alkylamines in water.[6,7] Especially, titanate solutions, in which the solute had the same structure as a titanate sheet obtained by the delamination of a layered titanate, $H_xTi_{(2-x/4)}\square_{x/4}O_4$ ($\square$: vacancy),[8] are very stable over many years and are free of halogens, alkaline cations and organic chelates. Titanate solutions can be prepared much more easily than by the conventional method, which comprises multiple steps, such as a solid-state reaction of TiO_2 with $CsCO_3$, the ion exchange of Cs^+ with H^+ and the delamination of $H_xTi_{(2-x/4)}\square_{x/4}O_4$ using tetrabutylammonium hydroxide (TBAOH) or ethylamine.[9] In the near future, these pure aqueous titanate solutions will become much important not only for environmental considerations, but also for the fabrication of functional ceramics requiring high purity. A film prepared from the TIP–TMAOH sol was found to crystallize to anatase at temperatures as low as 350 °C with a refractive index of 2.40 at 600 °C; It was also found that a small amount of sucrose (3 mol% to Ti) added to the sol made the resultant film drastically uniform.[10] Furthermore, when a film prepared from the sol containing 30 mol% of sucrose to Ti was irradiated through a patterning mask and subsequently heated in air at 500 °C, it was found that the irradiated part of the film selectively turned dark brown.

There are many reports regarding the preparation and characterization of a delaminated titanate suspension: synthesis,[11–13] ion-exchange property of the film,[14] intercalation of polymer,[15,16] swelling of the layered film,[12,17,18] photocatalytic property,[19,20] and fabrication of Langmuir–Blodgett (LB) films.[21,22] To our knowledge, there is no report relating to any change in the properties of the layered titanate films themselves by photoirradiation, although the densification of TiO_2 gel films derived from the hydrolysis of TIP was published.[23] In this paper, the effect of photoirradiation on the change in the hardness, thickness and refractive indices of the titanate film, and the behavior of coloring by sucrose was investigated.

Experimental

Chemical Reagents. Titanium tetraisopropoxide ($Ti(OPr^i)_4$: TIP, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used after distillation under reduced pressure. Commercial extrapure reagents, tetraethyl orthosilicate ($Si(OEt)_4$: TEOS), diethylamine (Et_2NH), triethylamine (Et_3N), aqueous solution of tetramethylammonium hydroxide (15%, TMAOH), were used as received from Wako Pure Chemical Industries, Ltd., Osaka, Japan. An aqueous solution of choline ((2-hydroxyethyl)trimethylammonium hydroxide, 48–50%, Tokyo Kasei Kogyo Co. Ltd.) was also used instead of TMAOH.

Preparation of Layered Titanate Films. The preparation of aqueous titanate solutions from TIP was performed as reported previously.[6–7] The molar ratios of TMAOH, choline, alkylamines or chelating ligands to Ti are denoted by R henceforth. Thus, 1.2 M TIP–TMAOH ($R = 0.4$), 1.0 M TIP–choline ($R = 0.4$), 0.7 M TIP–Et_2NH ($R = 0.5$), 0.8 M TIP–Et_3N ($R = 0.5$) and 1.0 M TEOS–TMAOH ($R = 0.5$) were prepared. A small amount of sucrose (3 mol% to Ti) was added to the solution in order to improve the film uniformity.[10] It was confirmed that its addition up to 30 mol% did not affect the interlayer distance of titanate layer compounds and the crystallization temperature of anatase.

The films were prepared on either borosilicate glass (Corning Inc, #7059) or SiO_2 glass (Nippon Silica Glass) by a spin-coating method (6000 rpm, 30 s). The film was irradiated by a 500-W super high-pressure mercury lamp (Ushio Denki Co., Ltd.) through water as an IR-cut filter. The irradiation power density through the filter was 0.4 W cm^{-2}. In a heat treatment of the coated titanate films, the films were directly introduced into a horizontal furnace electrically heated at a given temperature, and then heated for 30 min in air.

Characterizations. All characterizations were performed for single-coated films. XRD patterns (Model Geigerflex, Rigaku Co., Tokyo, Japan) were recorded using graphite monochromated Cu $K\alpha$ radiation with a scanning speed of 2°/min over the 2θ range of 2°–70°. The thickness and the refractive index of films were measured by an ellipsometer (DVA-36VMW, Mizojiri Optical Co., Ltd.) equipped with a He–Ne laser (632.8 nm), and a UV–vis spectrometer (Hitachi U-3500). The carbon content of the film was analyzed by Electron Spectroscopy for Chemical Analysis (ESCA, Shimadzu ESCA-850). Infrared (IR) spectra of the powder scraped away from the photoirradiated films on a glass plate were recorded with a spectrophotometer (PERKIN-ELMER System 2000 FT-IR) in the 4000–400 cm^{-1} wavenumber range (KBr method). Liquid-state ^1H-NMR spectra (Model FT-NMR alpha-400, JOEL, Tokyo) were measured at room temperature under an external magnetic field of $H_0 = 9.4$ T with an internal standard of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). The specimens were mixed with D_2O in a sample tube with a diameter of 5 mm.

Determination of Film Hardness. The film hardness was measured by a pencil method,[24] in which Mitsubishi Hi uni pencils (hardness: 6B-6H) were used.

Patterning of Films Prepared from Titanate Sols. The gel film prepared from the titanate sols was irradiated through a patterning mask for 30 min, leached in water and finally fired at 500 °C for 30 min in air. Similarly, a film prepared without leaching process was also examined.

Results

Properties of the 1.2 M TIP–TMAOH ($R = 0.4$) Sol and the Films Prepared from the Sol. The aqueous sol of 1.2 M TIP–TMAOH ($R = 0.4$, sucrose 3 mol%) contains about 37 vol% 2-propanol resulted from the hydrolysis of TIP. The sol remained stable even after evaporating the alcohol. The presence of 2-propanol did not affect the results obtained in this study. Therefore, in this paper, the sol was used as it was prepared without the evaporation of 2-propanol.

Figure 1a shows the XRD patterns of films prepared from the TIP–TMAOH sol. The film dried at 100 °C had a broad diffraction peak below 5°. The peak became slightly sharp at 200 °C, but again broad at 300 °C. Finally, the film crystallized to anatase at 350 °C. The crystallite size of the anatase film fired at 400 °C was estimated to be 14 nm from the peak width of the (101) reflection of anatase using Scherrer's equation. A film prepared at 100 °C seemed to be almost amorphous by XRD. However, in our previous report, Raman spectra revealed that the solute (or colloid) was a layered titanate,[7] indicating that the species consisted of a short-range order. Actually, when titanate films were coated using the clear sol refluxed for 3 h, a distinct diffraction pattern of the layered structure was found, as shown in Fig. 1b. Three sharp peaks located at 5.16° (1.71 nm), 10.36° (0.85 nm) and 14.90° (0.59 nm) were clearly observed at 100 °C. The pattern is similar to that reported for delamination of the layered titanate, $H_xTi_{(2-x/4)}\square_{x/4}O_4$ ($\square$: vacancy).[8] However, in the case of titanate films prepared from refluxed sols, crystallization to anatase was observed at 550 °C, which was higher than that of the film from the sol without reflux. It was inferred that the crystallization to anatase was difficult, since the framework of the layered structure might be built by reflux.

A decrease in solubility toward water was observed for a film fired at 200 °C, but the film was soluble in aqueous TMAOH (15%). However, films heated above 350 °C, which were composed of anatase, were insoluble in both water and aqueous TMAOH.

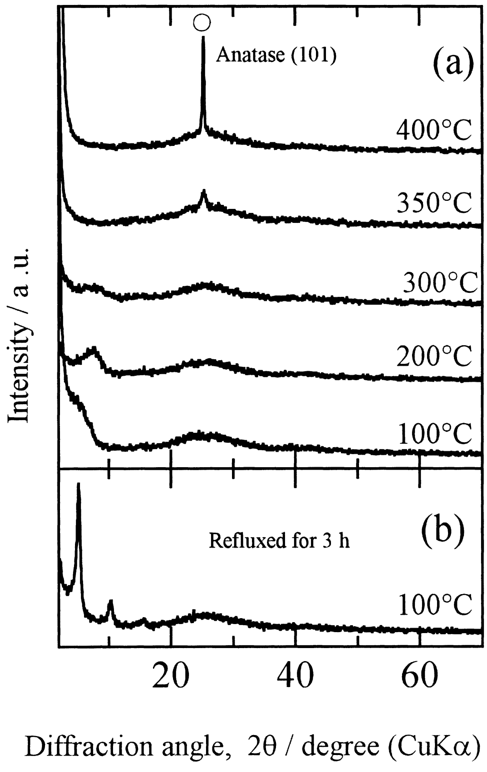

Fig. 1. XRD patterns of the thin films prepared from (a) 1.2 M TIP–TMAOH ($R = 0.4$, sucrose 3 mol%) and (b) 1.2 M TIP–TMAOH ($R = 0.4$, sucrose 3 mol%) refluxed for 3 h.

Effect of Photoirradiation to the Films. Figure 2 shows the variations in the XRD patterns of the films for various UV irradiation time durations. The films were prepared from the refluxed TIP–TMAOH sol. Since the films were prepared from the refluxed sol, as described above, the unirradiated film exhibited distinct diffraction peaks. After photoirradiation for 20 min, the clear diffraction patterns was broadened and shifted to higher angles, indicating that the interlayer distances decreased. The *d* value (at 9.40°) for the film irradiated for 30 min was 0.94 nm, being in good agreement with the (020) reflection of $H_xTi_{(2-x/4)}\square_{x/4}O_4{\cdot}H_2O$. This observation strongly suggests that the TMA^+ ions located between the titanate layers were photochemically decomposed. After irradiation for 60 min, the film became almost amorphous.

When the film was irradiated with light at a wavelength above 300 nm through a cut filter, the film was dissolved in water and no changes in the solubility to water and refractive index were observed, regardless of the irradiation time. However, when irradiated with light at a wavelength below 300 nm for 20 min or longer, the film became insoluble in water, but still soluble in aqueous TMAOH (15%). Accordingly, it is concluded that the film had a photosensitivity below 300 nm and the layered structure was changed by photoirradiation.

When a film prepared from the refluxed TIP-TMAOH sol was heated after photoirradiation, its crystallization to anatase was not found until 500 °C.

On the other hand, films derived from commercial sols, STS-01 and STS-21 (Ishihara Sangyo Kaisha, Ltd., Osaka, Japan) containing crystalline TiO_2 (anatase, $d = 9$ nm) did not exhibited any change in solubility after photoirradiation, and opaque films were obtained; they dissolved in both water and the TMAOH solution, even after photoirradiation. These results indicate that the titanate solution is completely different from a simple colloidal TiO_2 suspension.

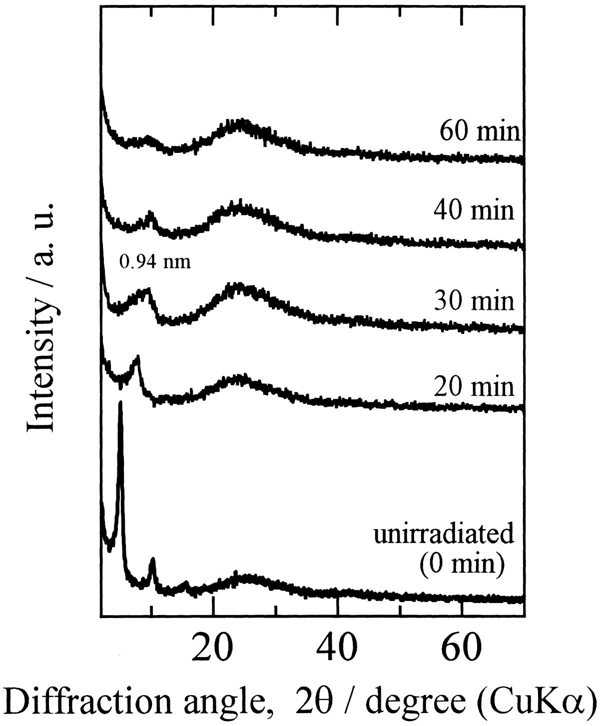

Fig. 2. Effect of photoirradiation on XRD patterns of the thin films prepared from 1.2 M TIP–TMAOH ($R = 0.4$, sucrose 3 mol%) refluxed for 3 h.

Effect of Photoirradiation on the Hardness and Refractive Indices of the Titanate Films. Figure 3 shows the changes in the hardness and refractive indices of the TIP–TMAOH films with the irradiation time. The hardness data of the films prepared from an alcoholic solution of the TIP–DEA, which were irradiated for 0 and 40 min, are also included for a comparison. For TIP–TMAOH films, an abrupt increase in the hardness and refractive index was observed after 20 min of irradiation in accordance with the result of a decrease of the solubility to water. The films irradiated for longer than 30 min were hard (hardness 2H) with refractive indices of 1.95 to 1.98. This observation suggests that densification, a decrease of the solubility and hardening of the film simultaneously occurred with photoirradiation for about 20 min. The TIP–DEA films were much softer than the TIP–TMAOH films, even after 40 min of irradiation, as can be seen from Fig. 3.

Similarly, the changes in the hardness and refractive indices of the TIP–TMAOH films upon a heat treatment were examined as shown in Fig. 4. A remarkable change in the hardness was observed between 200 and 250 °C, and a decrease in solubility was observed at 200 °C or above. The refractive indices of the films rapidly increased up to 350 °C, at which point crystallization to anatase was detected by XRD, as shown in Fig. 1a. On the other hand, the TIP–DEA film had already become hard at 200 °C, suggesting that the hydrolysis and condensation of the DEA-chelated TIP progress well by heating in air.

Figure 5 shows the effects of photoirradiation and a heat treatment on the thickness and refractive index of TIP–TMAOH films. The thickness and refractive indices were calculated by both ellipsometry and UV–vis spectroscopy. Along with the heating temperature, the thickness of both irradiated and unirradiated films decreased, and became almost constant

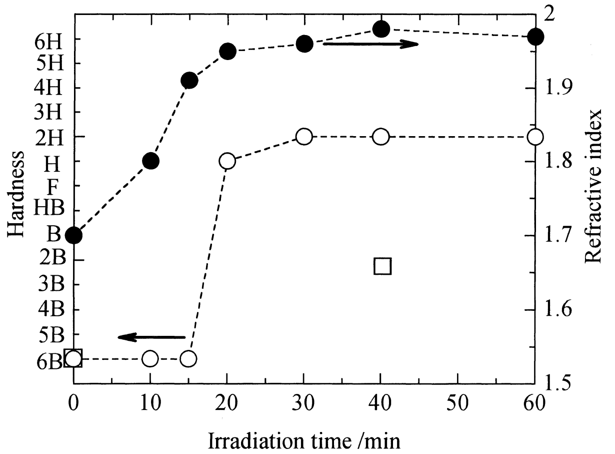

Fig. 3. Changes in the hardness and refractive indices of the TIP–TMAOH films on irradiation time. ○: hardness of the films; ●: refractive indices of the films; □: hardness of the films prepared form 2-propanol sol of 0.5 M TIP–DEA ($R = 2$).

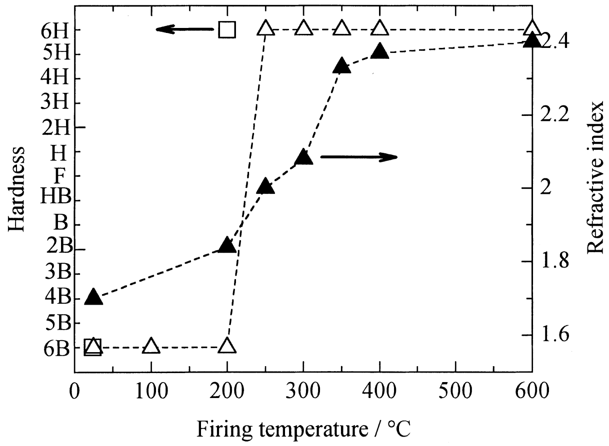

Fig. 4. Changes in the hardness and refractive indices of the TIP–TMAOH films on heat treatment. △: hardness of the films; ▲: refractive indices of the films; □: hardness of the films prepared form 2-propanol sol of 0.5 M TIP–DEA (R = 2).

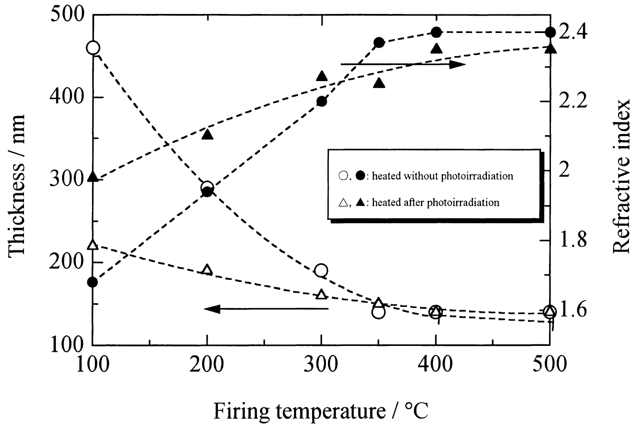

Fig. 5. Effects of photoirradiation and heat treatment on thickness and refractive index of the films, which were prepared from 1.2 M TIP–TMAOH (R = 0.4, sucrose 3 mol%).

above 400 °C. The reduction in thickness of the films upon a heat treatment was rather small in irradiated films. The refractive indices of the irradiated films were larger than that of the unirradiated films up to 300 °C, but were reversed above a certain temperature, being 2.35 and 2.40 at 400 °C for irradiated and unirradiated films, respectively.

IR and Liquid NMR Measurements. In order to investigate the change in the film caused by photoirradiation, IR spectra were recorded. Figure 6 shows the IR spectra of a powder obtained from films prepared from 1.2 M TIP–TMAOH (R = 0.4). The results of a powder prepared from 1.5 M TEOS–TMAOH (R = 0.5) sol are also shown for a comparison. For a powder prepared from the TIP–TMAOH film, two absorption bands were clearly observed around 950 and 1500 cm^{-1} regions, which are assignable to the stretching vibration of the C–N bonds and the bending vibration of the C–H bonds in TMA$^+$, respectively. After 30 min of irradiation, these bands completely disappeared, indicating that TMA$^+$ in the film was decomposed by UV irradiation. The powder obtained from the TIP-choline film revealed a similar decomposition behavior. On the other hand, the powder obtained from the TEOS–TMAOH film did not show any change in the IR spectra by photoirradiation, suggesting that the titanate layers play a crucial role in TMA$^+$ decomposition.

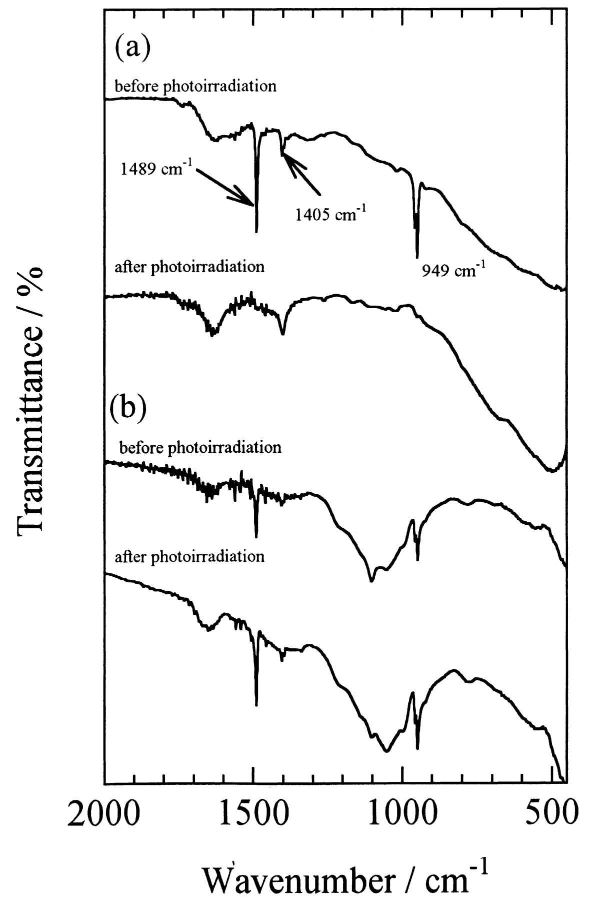

Fig. 6. IR spectra of the powder prepared from aqueous sols of (a) 1.2 M TIP–TMAOH (R = 0.4) and (b) 1.5 M TEOS–TMAOH (R = 0.5). The films were dried at room temperature and photoirradiation was carried out for 30 min.

A liquid NMR measurement was performed in order to detect the decomposition products formed by photoirradiation. The titanate solution was put in a silica test tube and photoirradiated with stirring for 1 h. In a TIP-choline solution, trimethylamine was detected, indicating that (2-hydroxyethyl)trimethylammmonium ion (choline) was decomposed by photoirradiation in the titanate sol to yield trimethylamine. In the case of the TIP–TMAOH sol, no clear decomposition products were detected by NMR spectroscopy.

Patterning of a Titanate Film Using Photoirradiation. The results described above indicate that irradiated films became hard and insoluble in water, and that patterning of the film might be possible. Figure 7a shows a patterned TiO_2 film, which was prepared from TIP–TMAOH (R = 0.4, sucrose 3 mol%) by leaching the film after photoirradiation for 30 min through a mask pattern, and subsequently heating at 500 °C for 30 min. A negative pattern of the mask was clearly observed. In the same manner, patterning was possible in the TIP–cho-

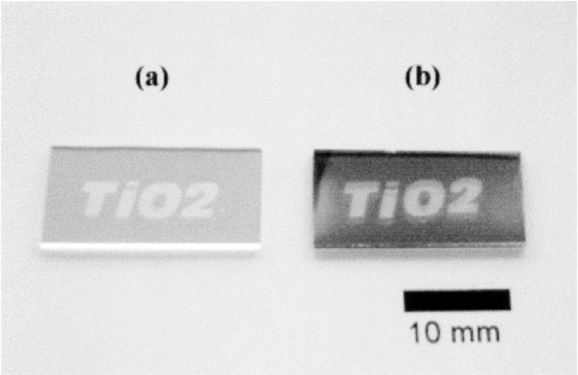

Fig. 7. Photographs of the patterned anatase films, which were prepared from the 1.2 M TIP–TMAOH (R = 0.4, sucrose 3 mol%) sol, followed by firing at 500 °C for 30 min. (a) The unirradiated part of the film was removed by leaching and (b) The film was fired without leaching process. The irradiated part of the film was colored and amorphous, and unirradiated part of the film was anatase.

line, TIP–Et_2NH and TIP–Et_3N systems, but impossible in TEOS–TMAOH. In the TIP-choline system, the film became insoluble within 5 minutes of irradiation with the generation of a strong amine odor, being in good agreement with the NMR result.

When the film was made from titanate sols containing 30 mol% sucrose, the irradiated part of the film was insoluble as well, but readily peeled off by soaking the film in water. Hence, the irradiated film was directly fired at 500 °C in air without any leaching process. Interestingly, it was found that only the irradiated part of the film became colored dark brown, as shown in Fig. 7b. The colorless and colored parts of the film were found to be anatase and amorphous by XRD, respectively. Carbon was detected in the colored part of the film all over depth direction by XPS, which is shown in Fig. 8. A further heat treatment at this temperature for more than 30 min made the colored film colorless, and led to the crystallization of anatase. This may have been due to the fact that the full decomposition of sucrose was rather difficult in the irradiated part of the film.

A wide variety of polyhydroxy compounds was examined in place of sucrose. However, only sucrose and raffinose, which are di- and tri-saccharides, were effective for the coloring. The coloring of the irradiated film was not observed in the TIP–Et_2NH, TIP–Et_3N and TEOS–TMAOH systems.

Discussion

Comparison of Photoirradiation with a Heat Treatment in Views of a Decrease in the Solubility, Hardness, and Crystallization to Anatase. The decomposition behaviors of layered titanate films prepared from 1.2 M TIP–TMAOH (R = 0.4, sucrose 3 mol%) sol by photoirradiation and a heat treatment can be illustrated as in Fig. 9; several of their properties are summarized in Table 1.

Photoirradiation to the titanate films can decompose the TMA^+ in the interlayer, but not accelerate crystallization to anatase, while a heat treatment of the titanate films can lead to anatase along with the decomposition of TMA^+.

Refluxing the sol did not influence the properties of the film, such as refractive index, thickness, hardness and patterning by photoirradiation and heat-treatment, although the crystallization temperature to anatase became higher than that of the film from the sol without reflux.

Once the TMA ions located between the layered titanates are decomposed by photoirradiation, the interlayer distance

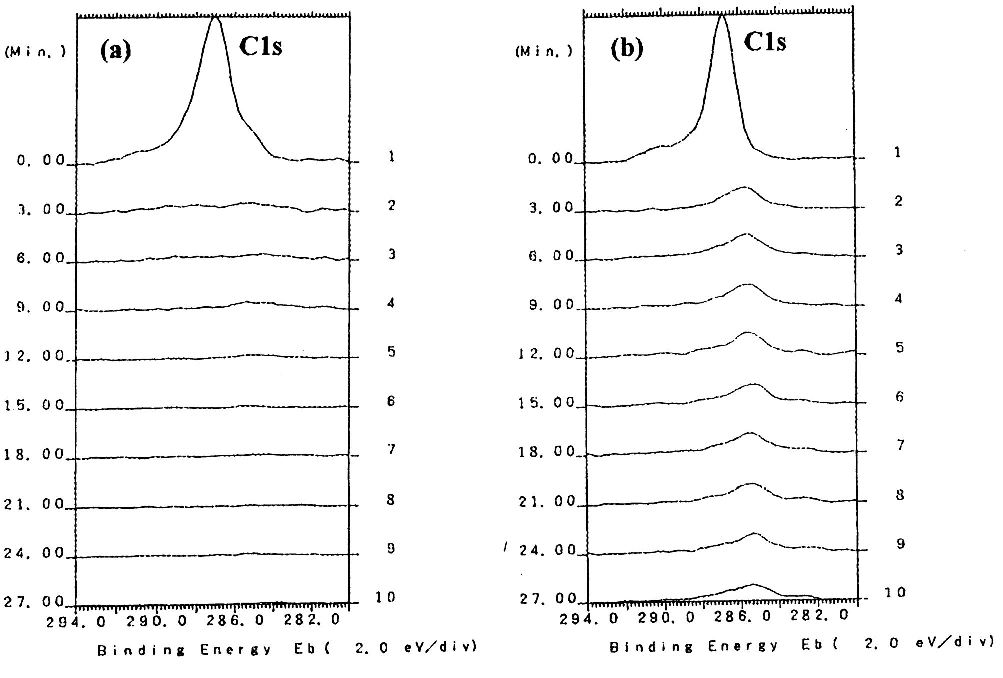

Fig. 8. ESCA depth profiles of the (a) unirradiated and (b) irradiated films, which were prepared from the 1.2 M TIP–TMAOH (R = 0.4, sucrose 30 mol%) sol, followed by firing at 500 °C for 30 min.

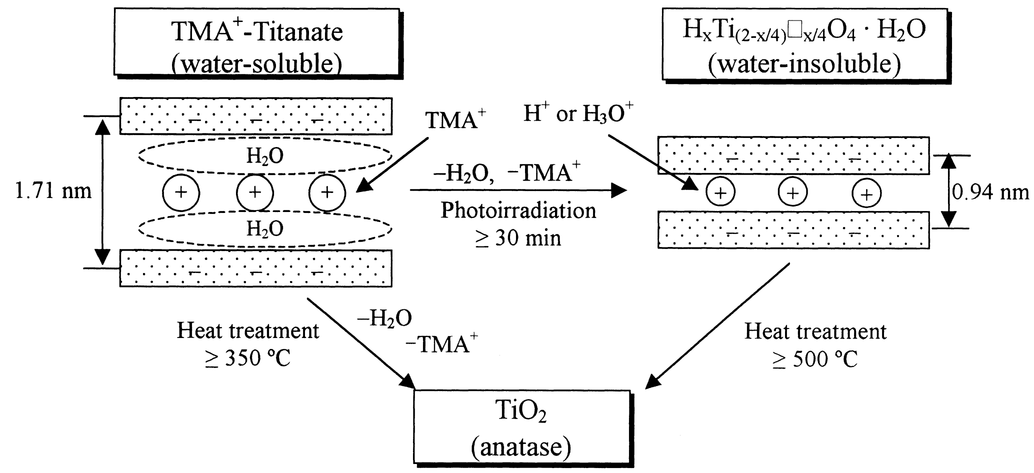

Fig. 9. The decomposition, decrease of solubility and densification of the gel films under photoirradiation and heat treatment.

Table 1. Comparison of the Irradiated with Heat Treated Films

1.2 M TIP–TMAOH (*R* = 0.4, sucrose 3 mol%)	Photoirradiation	Heat treatment (without irradiation)	Remarks
Decrease in solubility	20 min	200 °C	
Hardness	H (20 min)	6B (200 °C)	6H[a] (250 °C)
Crystallization to anatase	500 °C	350 °C	
Refractive index	2.35 (500 °C)	2.37 (350 °C)	2.40[a] (500 °C)

The values in parentheses are irradiation time or firing temperature that the film was prepared. a) in the case of heat treatment.

would contract from 1.71 to 0.94 nm, since the size of H^+ or H_3O^+ located between the layers is rather small compared to TMA^+, leading to a compound which is similar structure to $H_xTi_{(2-x/4)}\square_{x/4}O_4\cdot H_2O$. This formation of the protonated titanate is thought to be the main reason for the hardening, densification and decrease of solubility in water. In addition, it is reported that the protonated titanate can be dissolved or delaminated only in a highly basic aqueous solution, such as tetrabutylammonium hydroxide (TBAOH) and ethylamine.[8,9] The fact that the irradiated film was insoluble in water, but soluble in aqueous TMAOH, is in agreement with the property of the protonated titanate.

On the other hand, such photo-densification was not found for a film prepared from aqueous suspensions of crystalline TiO_2 (anatase), indicating that the layered titanate sols are much different from the simple TiO_2 suspension with respect to the structure and photosensitivity of colloids.

Patternability and Coloring of a Patterned Film by Sucrose. All of the layered titanate films used in this study were transparent (more than 90%) above 320 nm, and the transmittance at 300 nm was about 55%. The change due to photoirradiation was observed when the film was irradiated by light below 300 nm. It is reported in several papers that the λ_{max} of a suspension and film prepared from $H_xTi_{(2-x/4)}\square_{x/4}O_4\cdot H_2O$ was estimated to be 265 to 268 nm, and that the absorption started around 300 nm. Accordingly, the absorption of the film is assignable to that of the layered titanate, and the photocatalytic reaction of the titanates can occur at wavelengths below 300 nm. In the case of TEOS–TMAOH, the film was not affected by UV irradiation because it was transparent in the region of the light from a super high-pressure mercury lamp.

Coloring by polyhydroxy compounds was observed for only sucrose and raffinose, which are di- and tri-saccharides, respectively. Since the saccharides can be regarded as being carbon hydrates $C_x(H_2O)_y$, they may easily lose water to leave carbon when heated. As a matter of course, the photodecomposition of saccharides may occur, but it is thought that their excess amount in the layered titanate could not be completely decomposed after 30 min of irradiation. Actually, when sol containing 3 mol% of sucrose was photoirradiated, it turned yellow, indicating that photodecomposition might occur.

The type of starting sols is also related to the coloring of the irradiated film. Coloring occurred in films prepared from the aqueous sols from TIP–TMAOH and TIP–choline, while aqueous sols from TIP–Et_2NH and Et_3N, 1.0 M TIP–LA–NH_3 (R = 1, 1) and TEOS–TMAOH were not observed. The films prepared from TIP–TMAOH and TIP–choline clearly showed a layered structure, and had refractive indices of 1.95 to 1.98 after photoirradiation, while films from TIP–Et_2NH and Et_3N had very broad peaks assignable to a layered structure by XRD and Raman, and had a lower refractive index (~1.8) even after photoirradiation. Films obtained from the TEOS–TMAOH system had no photosensitivity, as expected, and had a refractive index of about 1.4. A film prepared from TIP–LA–NH_3 was amorphous, but photosensitive. These results indicate that the presence of a well-defined, dense layered structure can be a crucial factor of this coloring. Therefore, it is thought that sucrose molecules were confined within the host titanate layers densificated by UV irradiation, and that the oxidation of the sucrose by oxygen in air was difficult under heating because the densificated titanates suppressed the diffusion of oxygen.

In the TIP–choline system, the film became insoluble within 5 minutes of irradiation, while 20 minutes were required for the TIP–TMAOH system. TEOS–TMAOH did not show any change in the film property, and remained soluble after long-time photoirradiation. It is evident that the layered titanates have photocatalytic activity, and that (2-hydroxyethyl)trimethylammmonium ion in titanate is photocatalytically decomposed much faster than TMA^+.

It can be assumed that the difference in the decomposition rate between TMA^+ and (2-hydroxyethyl)trimethylammmonium is partly related to their chemical structures. For example, it is possible to considerate that choline is decomposed to generate trimethylamine in the same manner as Hoffmann degradation (eliminatnion).[25] The degradation may proceed by an E2 reaction, that is, a thermal decomposition of quarternary ammonium hydroxides with a β-hydrogen atom, as viewed from nitrogen atom to yield alkenes, tertiary amines and water. According to this degradation reaction, it can be thought that choline with a β-hydrogen atom is decomposed faster than a TMA ion that has no β-hydrogen atom. Therefore, it is thought that the photocatalytic degradation reaction of choline can also occur faster than that of TMA^+.

The alcoholic sol of the TIP–DEA and aqueous sol of the TIP–LA–NH_3 system also have photosensitivity. The DEA and LA are known to make chelate compounds with Ti. Photoirradiation can break the Ti–O bonds in the chelate by LMCT. As a result, Ti^{4+} is destabilized and hydrolyzes to form an insoluble Ti–O–Ti polymer, but the extent of the polymerization would be lower than that takes place in the titanates.

Conclusions

It was found that the alkylammonium ions between layered titanates could be decomposed by photoirradiation to lead to a decrease in the interlayer distance, hardening and densification of the films. Although photoirradiation did not accelerate the crystallization of anatase, the film became insoluble in water, and had a high refractive index of around 2.0 and a hardness of 2H, indicative of some applicability as a surface modifier of plastics, etc. The addition of a large amount of sucrose to titanate sols made it possible not only to improve the film uniformity, but also to draw a pattern in the films.

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