

TEMPERATURE PROGRAMMED DESORPTION ANALYSIS OF SOL–GEL-DERIVED TITANIA FILMS

Design of a sol preparation procedure

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Sol–gel-derived titania films were analyzed by temperature programmed desorption (TPD) and X-ray diffraction (XRD) techniques. The relationship between the TPD curves measured for two types of titania gel films and their crystal structures was investigated. On the basis of the analyses, a preparation process for a titania sol solution containing anatase nanocrystals was designed and developed. Using this process, a colloidal anatase titania sol solution was prepared by heating aqueous titanium hydroxide containing HCl at 60°C for 2 h. The nanocrystal structure of the titania films obtained by coating the sol on glass substrates was confirmed by TPD and XRD measurements.

Keywords: anatase, photocatalysis, temperature programmed desorption, thin film, titania

Introduction

Titania (TiO₂) films have been widely investigated for various applications such as optical, electrical, and especially photocatalytic uses. Anatase titania films in particular are known for their high photoactivity [1–4]. Titania films have been fabricated by many processes, including dry physical ones such as sputter and vapor-phase deposition techniques, which require a high vacuum system and consume a lot of energy [5]. In recent years, wet chemical processes [6] such as the sol–gel method [7], soft-solution processing [8] and liquid phase deposition [9] have been developed for fabricating titania films.

In conventional sol–gel processes, titania sol solutions are prepared by dissolving titanium alkoxides in alcohol solvents, followed by hydrolysis using H₂O and an acid. Anatase films are obtained by firing gel films coated with the sol solutions on substrates. These processes require no vacuum apparatus, are simpler and more convenient and consume less energy than their dry counterparts. However, the processes generally include a firing process to burn organic components and densify and crystallize metal oxides in the coating films.

In recent years, nanocrystalline titania films have been fabricated in an aqueous solution [10–20]. In this process, starting materials such as titanium tetraisopropoxide, TiCl₄, Ti(SO₄)₂ and titanium hydroxide are reacted in an aqueous acidic or basic solution with heating to obtain titania crystals. However, not only anatase but also other polymorphs like rutile and brookite and their mixtures can be prepared by

changing the starting materials, acidity (basicity) or heating conditions. Colloidal anatase solutions for coating films have been fabricated only in a few studies [10–12], although crystal powders have been prepared in a number of investigations [13–20].

Temperature programmed desorption (TPD) is an excellent technique for analyzing not only adsorbed gases on the surface of bulks and films [21, 22] but also formation processes and components of metal oxide thin films [23–28]. Sawada *et al.* reported TPD curves of fluorine-doped tin dioxide (FTO) films prepared by a pyrosol technique using solutions with different F-doping concentrations. The principal evolved gases from the FTO films were H₂O (*m/z* 18), CO (*m/z* 28) and CO₂ (*m/z* 44). The intensity of the fluorine (*m/z* 19) TPD curves was very strong for the highly F-doped films at temperatures above 400°C [23–25]. We have used TPD to investigate the firing processes of sol–gel-derived titania films obtained from different Ti sources, specifically, Ti(OC₂H₅)₄ and TiCl₄, and found that the components and the crystallizing temperature of the gel films differed depending on the Ti sources used [26]. We have also analyzed the ultraviolet (UV) hardening process of hafnia films containing formic or oxalic acid by the TPD technique and reported that the amount of acid decreased after UV irradiation, followed by hardening [27, 28].

Such TPD studies of thin films reveal the relationship between the composition and crystallization temperature of the films and their preparation procedures. Based on the TPD results, a sol solution preparation procedure can be designed for obtaining metal oxide films.

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In this work, the relationship between the TPD curves found for titania gel films obtained by a sol-gel procedure and their crystal structure was studied. On the basis of the results, a titania sol solution containing anatase nanocrystals was designed and prepared in an aqueous solution. The titania films coated with the sol solution were analyzed by TPD, XRD and transmission electron microscope (TEM) techniques. The photoactivity of the films was also evaluated.

Experimental

Preparation of titania sol solutions and films

Titania gel films (T-1 gel films) were prepared from titanium tetraethoxide as follows. A mixture of H₂O (0.36 g) and 35% HCl (0.15 g, $1.4 \cdot 10^{-3}$ mol) was added to titanium tetraethoxide (Ti(OC₂H₅)₄) (4.56 g, 0.02 mol) in a 99.5% ethanol (40 mL) solution under a N₂ atmosphere. The mixed solution was held at ambient temperature for one day to obtain the T-1 titania sol solution. Transparent T-1 gel films were then obtained by spin-coating the sol solution on silicon wafer substrates (Sumco Corporation) at a spinning rate of 2000 rpm for 30 s.

T-1 fired films were prepared by firing the T-1 gel films at 550°C for 30 min.

Other titania gel films (T-2 gel films) were fabricated from titanium tetrachloride. A titania sol solution (T-2 sol solution) was prepared by adding 35% HCl (0.017 g, $1.6 \cdot 10^{-4}$ mol) to a solution of titanium tetrachloride (17.6 g, $9.3 \cdot 10^{-2}$ mol) in H₂O (10.0 g) under a N₂ atmosphere. The mixture was then held at ambient temperature for one day. Transparent T-2 gel films were then obtained by the same process used for the T-1 gel films.

Titania films (T-3 coating films and T-4 films) were fabricated as follows. Titanium tetrachloride (3.52 g, $1.9 \cdot 10^{-2}$ mol) was dissolved in H₂O (20 g) in a N₂ atmosphere. To the solution, 29% aqueous ammonia (5.6 g) was added to precipitate titanium hydroxide, and the precipitate was washed with water to a level of pH 7 of the filtrate. To the precipitate, H₂O (20 g) and 35% HCl (0.78 g, $7.5 \cdot 10^{-3}$ mol) were added to adjust it to pH 1, followed by heating at 60°C for 2 h to obtain a T-3 colloidal titania sol solution. T-3 coating films were prepared by coating the colloidal solution on silicon wafer substrates (Sumco Corporation) and alkali-free glasses (AF-45, Schott Glass) by the same process used for the T-1 gel films.

T-4 films were prepared by applying ultraviolet (UV) irradiation to the T-3 coating films for 10 min using a high-pressure mercury lamp (H1000L, Toshiba Lighting and Technology Corp.). The temperature of the film surface under UV irradiation was about 100°C.

Preparation of T-3 powder

T-3 powder was prepared by evaporating the T-3 sol solution at 60°C for 40 min using a rotary evaporator. This powder was used for X-ray diffraction (XRD) measurement.

Measurements

The crystal structures of the titania films and powders were determined with a Rigaku RAD-2 X-ray diffractometer using graphite-filtered CuK_α radiation. A Philips X'Pert MRD X-ray diffractometer was also used to determine the crystal phases of the films by grazing incidence X-ray diffraction (XRD) measurement.

TPD curves of the films were measured in a temperature range of 50–900°C at a constant heating rate of 20°C min⁻¹ under a pressure of 10⁻⁷ Pa with TPD equipment (EMD-WA 1000S/W, ESCO). The equipment consists of two vacuum chambers (a load-lock chamber and an analysis chamber), four vacuum pumps, an infra-red (IR) heating unit, a sample transfer unit and a quadruple mass spectrometer. The TPD measurement of a sample was carried out as follows. The analysis chamber was evacuated to a vacuum of 10⁻⁷ Pa using a turbo molecular pump together with an oil rotary pump. A film sample was transferred from the load-lock chamber by means of the sample transfer unit to a sample stage in the analysis chamber and heated at a constant heating rate of 20°C min⁻¹ with the IR heating unit in order to measure the TPD curves. A thermocouple was used to measure the surface temperature of the specimens, which were 47–100 nm in thickness and 1 cm×1 cm in size.

The microstructure of the T-3 powders was observed with a Hitachi HF 2000 transmission electron microscope (TEM).

The refractive index and thickness of the films were measured with a Mizojiri DHA-OLX ellipsometer employing a He-Ne laser (632.8 nm).

The photoactivity of the samples was evaluated by analyzing the degradation of an organic methylene blue dye in an aqueous solution, in which the titania films were immersed, under UV illumination at 302 nm using a Funakoshi Model UVM-57 spectrophotometer for 120 min. Absorbance of the initial and irradiated dye solutions containing the films was measured with a Shimadzu UV-2450 spectrophotometer.

Results and discussion

TPD curves of T-1 and T-2 gel films

TPD curves of the evolved species from the T-1 gel film were observed below 500°C. The curves corresponded to H₂O, ethanolato ligands coordinated to Ti ions,

HCl and their fragments, which were components or adsorbed species of the gel films.

The TPD curve of H_2O (m/z 18) evolved from the T-1 gel film in Fig. 1 shows a large asymmetric peak and a small symmetric one at approximately 100 and 225°C, respectively. The former peak is ascribed to the evolution of physisorbed H_2O because of the low desorption temperature and its asymmetric shape, whereas the latter one is attributed to the associated desorption of H_2O from Ti-OH in the gel film, the species of which were characterized by X-ray photoelectron measurement [26, 28, 29].

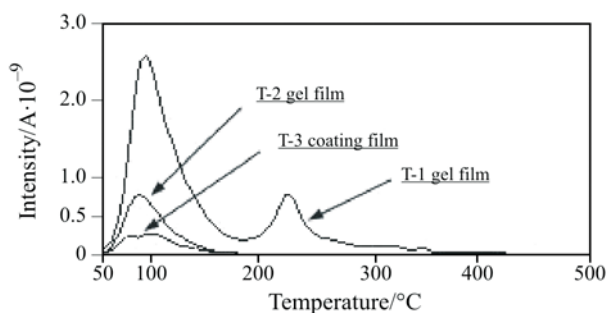


Fig. 1 TPD curves of H_2O (m/z 18) evolved from T-1 gel, T-2 gel and T-3 coating films

Although not shown in the figure, the TPD curve of $\text{C}_2\text{H}_5\text{OH}$ (m/z 44) evolved from the T-1 gel film showed a small peak at 210°C. The TPD curves of m/z 13, 14, 15, 26, 27, 28, 29 and 30 were also observed, all of which showed a large peak at 210°C and a small one at 335°C. These peaks are ascribed to the evolution of C_xH_y ($x=1$ and 2 , $y=1-6$) species generated from the ethanolato ligands, but containing the fragments of $\text{C}_2\text{H}_5\text{OH}$ and other C_xH_y ($x=1$ and 2 , $y=1-6$) species. After these fragments were eliminated, the real TPD curves of C_xH_y ($x=1$ and 2 , $y=1-6$) species obtained still showed a large peak at about 210°C and a small one at about 335°C [26]. These results indicate that ethanol and a large amount of C_xH_y ($x=1$ and 2 , $y=1-6$) species evolved from the ethanolato ligands at about 210°C and small amounts of the C_xH_y evolved at about 335°C. The latter peaks were caused by the crystallization to anatase from the amorphous phase in the gel film, which will be discussed next in terms of the TPD curves of HCl.

The TPD curve of HCl (m/z 36) evolved from the T-1 gel film in Fig. 2 shows peaks at the same temperatures as those of C_xH_y . This indicates that large amounts of organic components and adsorbed HCl of the T-1 gel film evolved at a temperature of about 210°C, and that smaller amounts evolved at about 335°C. The latter peak corresponds to the crystallization of titania gel to anatase, because the XRD pattern of the film fired at 300°C in the TPD

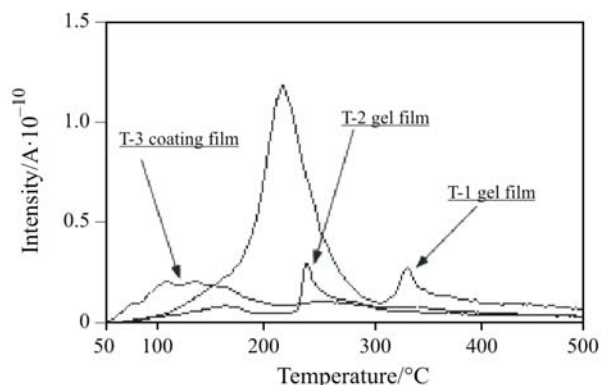


Fig. 2 TPD curves of HCl (m/z 36) evolved from T-1 gel, T-2 gel and T-3 coating films

apparatus showed only a reflection ascribed to the Si(111) substrate in the measured region, but the film fired at 400°C showed reflections ascribed to anatase [26, 30].

A large amount of organic moieties coordinated to Ti ions and adsorbed HCl evolved at about 210°C. The Ti and O ions in the T-1 gel film were then rearranged at the same time as or after the evolution of the small amounts of the organic components and HCl, which presumably were coordinated or adsorbed strongly, resulting in crystallization to anatase in form. It should be pointed out that the TPD peak of HCl at higher temperatures can be used as a favorable indicator of crystallization of titania films. Thus, monitoring the TPD curve of HCl evolved from titania gel films can lead to the design of a low-temperature procedure for obtaining anatase. It was also observed that the titania gel films containing organic groups crystallized in the high temperature region only after the organic species were eliminated. This suggests that titania gel films without organic groups can crystallize at lower temperatures than those with organic components.

TiCl_4 and H_2O were used respectively as a Ti source and a solvent to prepare the T-2 titania sol solution, which contained no organic groups. The sol solution was fabricated without heating, as was the T-1 sol solution. The T-2 gel film showed only TPD curves ascribed to the evolution of H_2O and HCl. The TPD curve of H_2O (m/z 18) evolved from the T-2 gel film in Fig. 1 shows only one peak at about 85°C, ascribed to physisorbed water, and no peak in the temperature region of 200–300°C indicating that no Ti-OH was present. The absence of organic groups is presumed to accelerate the interaction of Ti-OH groups in the gel film to form Ti-O-Ti bonding.

The TPD curve of HCl (m/z 36) evolved from the T-2 gel film in Fig. 2, however, shows a peak at about 240°C, although the temperature is lower than that of the T-1 gel film. This suggests that the T-2 gel film crystallized at a lower temperature than the T-1 gel film. T-2

gel films were fired in the TPD apparatus at 200 and 350°C to evaluate their crystallization temperature. The XRD pattern of the film fired at 200°C (Fig. 3a) shows only a reflection ascribed to the Si(111) substrate, but that of the film fired at 350°C (Fig. 3b) shows reflections due to anatase [30] (○), indicating that the titania in the T-2 gel film crystallized between 200 and 350°C. The crystallization temperature range is lower than that of the T-1 gel film because of the absence of organic groups. These TPD and XRD results indicate that the T-2 sol solution was composed of only Ti–O–Ti networks, though the structure was amorphous, which was due to the sol preparation condition without heating. These results indicate that the anatase crystal structure is obtained when the titania sol contains only Ti–O–Ti or Ti–OH–Ti networks and is prepared with heating.

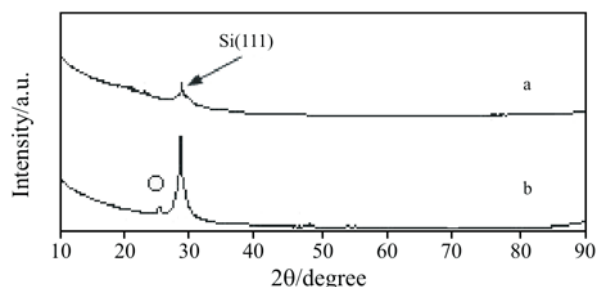


Fig. 3 XRD patterns of T-2 films fired at a– 200°C and b– 350°C in the TPD apparatus; ○– denotes anatase

TPD curves and crystal structure of T-3 coating film

In view of the foregoing results, the aqueous T-3 sol solution was prepared from titanium hydroxide, which was composed of only Ti–OH–Ti networks, and a HCl mixture under heating to accelerate crystallization. The T-3 coating films obtained were analyzed by TPD and XRD techniques. Only TPD curves ascribed to the evolution of H₂O, HCl and NH₃ were observed. The curves of H₂O and HCl evolved from the T-3 coating film in Figs 1 and 2 show only peaks below 100 and 200°C, respectively. The curve of H₂O is due to only physisorbed H₂O, as in the case of the T-2 gel film. This result indicates that the T-3 coating film did not contain Ti–OH moieties. The TPD curve of HCl differs from those of the T-1 and T-2 gel films. The absence of a peak over 200°C suggests that the titania sol and the coating film contained only titania crystals, which will be discussed in a later section.

The TPD curve of *m/z* 17 shown in Fig. 4 is too large to ascribe it only to the OH fragment of H₂O of the T-3 coating film and shows a different profile from that of H₂O (Fig. 1). It must have contained NH₃ and the OH fragment of H₂O since aqueous ammonia was used in the sol preparation procedure. The TPD curve calculated for NH₃ after the elimination of this

fragment is also shown in Fig. 4. The TPD curve of NH₃ was also calculated from that of *m/z* 15, which was the fragment of NH₃. The curve obtained was the same as that found by eliminating the OH fragment, thereby confirming that the curve was ascribable to NH₃. This assignment coincides with the result of the XRD analysis discussed later.

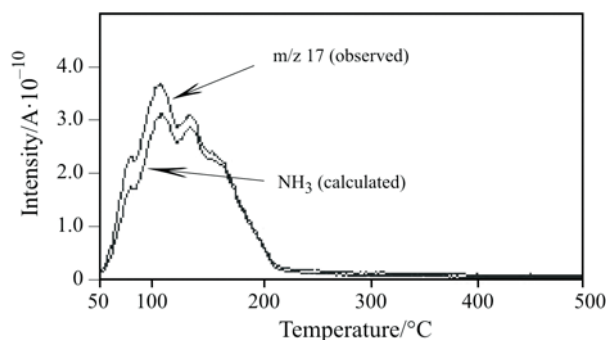


Fig. 4 TPD curves of *m/z* 17 (fine line) and NH₃ (bold line) calculated by eliminating OH fragment from observed curve of *m/z* 17

To clarify the crystal structure of the titania in the T-3 sol solution, the XRD pattern of the T-3 powder obtained from the T-3 sol was measured. The XRD pattern of the T-3 powder in Fig. 5 shows reflections (○) at $2\theta=25.2, 37.8, 47.5, 54.4, 63.0$ and 68.4° , indicating that the structure of the powder was anatase in form [30]. Observation of the pattern shape suggested that the powder had a nanocrystalline structure. Transmission electron microscope measurement of the powder revealed that the average size of the crystals was 5.5 nm. The reflections marked by the open triangles (△) are assigned to NH₄Cl that was formed in the sol preparation process and remained even after being washed with water. This result coincides with the TPD curves of NH₃ and HCl.

To confirm the structure in the T-3 coating and T-4 films, the XRD patterns of the films were measured by a grazing incidence XRD technique because of their thinness (47 nm in thickness). The XRD patterns of the T-3

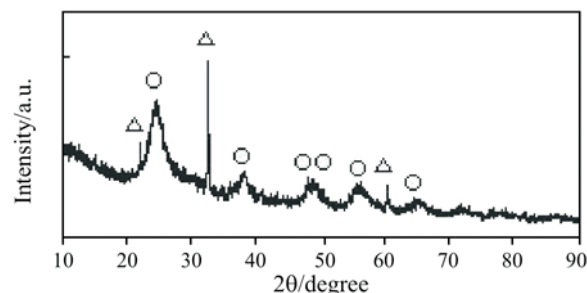


Fig. 5 XRD pattern of T-3 powder, ○ and △– denote anatase and NH₄Cl, respectively

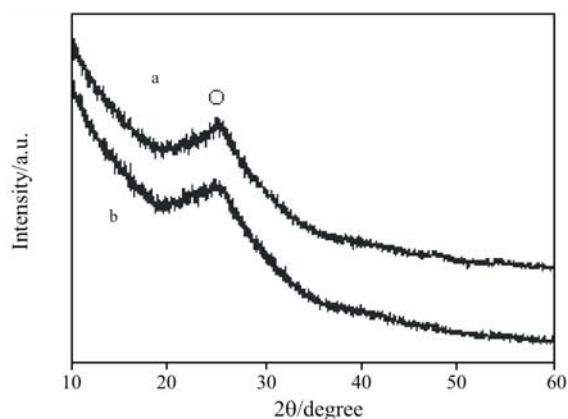


Fig. 6 XRD patterns of a– T-4 films and b– T-3 coating; ○– denotes anatase

coating film (Fig. 6b) and the T-4 film (Fig. 6a) show a small reflection (○) at about $2\theta=25^\circ$ due to anatase [30, 31]. These results indicate that the crystal structure of the T-3 coating and T-4 films was anatase, the same as the XRD result for the T-3 powder.

These XRD and TPD results imply that the T-3 sol solution contained anatase nanocrystals, which were fabricated by heating aqueous titanium hydroxide with HCl.

Photocatalysis of the titania films

The photoactivity of titania has been evaluated in many studies on the basis of the degradation of organic dyes, such as methylene blue, in water using UV illumination [1, 4].

The photoactivity of the films was tested by measuring the absorbance of an aqueous organic methylene blue dye solution, in which the T-1 fired film (obtained by firing the T-1 gel film), T-3 coating film and T-4 film were immersed, under UV illumination (302 nm) for 120 min. Changes in the peak absorbance of the dye solution during the reaction were measured and are shown in Fig. 7 where the values are indicated as a percentage of the initial absorbance. For comparison, a dye solution with no film was illuminated with the UV lamp and its absorbance (□) is also shown in the figure. However, the change between the initial and irradiated states was negligible. The absorbance (●) of the solution with the T-3 coating film, i.e., the coated sample of nanocrystalline anatase, decreased by 15% after 120 min of UV illumination. In the case of the T-4 film (▲), i.e., the coated sample of nanocrystalline anatase and UV-irradiated, the absorbance of the solution with the film decreased by 30%, whereas that (△) of the solution with the T-1 fired film, i.e., anatase obtained by firing the titania gel film at 550°C [31], declined by 24%. These results indicate that the T-3 coating film showed less

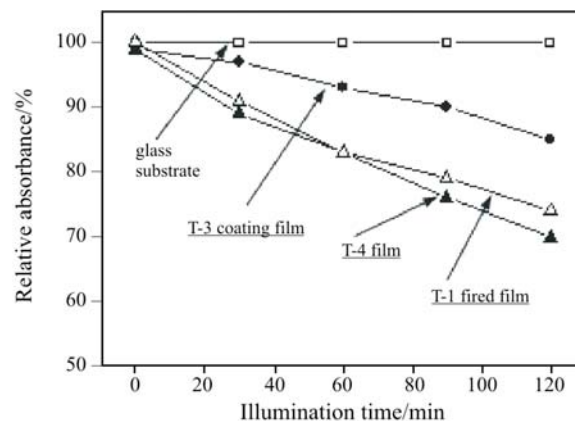


Fig. 7 Change in absorbance of aqueous methylene blue solutions immersed with T-1 fired, T-3 coating and T-4 films. The values are normalized to 100 at each initial state. △, ●, and ▲ denote T-1 fired, T-3 coating and T-4 films, respectively; □– denotes the absorbance of an aqueous methylene blue solution without any titania film

photoactivity than the T-1 fired film obtained by the conventional sol-gel method. However, the photoactivity of the T-4 film was the same as or slightly better than that of the T-1 fired film. The refractive index and film thickness of the T-3 coating film were 2.001 and 72 nm, respectively, whereas the T-4 film showed a higher refractive index of 2.069 and lower thickness of 61 nm. These results indicate that the T-4 film was denser than the T-3 coating film, since the former was prepared from the latter by UV irradiation with heating. The reason for the higher photoactivity of the T-4 film than that of the T-3 coating film is attributed to the former film's higher density than that of the latter.

Conclusions

The results of this investigation revealed that titania sol solution preparation procedures and the crystal structure of the titania in the sol solutions can be tailored on the basis of TPD and XRD analyses of titania gel films. The TPD curves ascribed to the evolution of HCl from the titania gel films were also found to be a good indicator of the crystallization of the titania. On the basis of the TPD results for two types of titania gel films, a colloidal anatase titania sol solution was designed and successfully prepared from aqueous titanium hydroxide containing HCl with heating at 60°C for 2 h. The nanocrystalline structure, which was formed in the sol preparation procedure, was confirmed by TPD, XRD and TEM analyses. The titania films coated with the sol showed high photoactivity under UV illumination.

Acknowledgements

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