Titanium (IV) Oxide Thin Films Prepared from Aqueous Solution

Shigehito Deki, Yoshifumi Aoi, Osamu Hiroi, and Akihiko Kajinami
Department of Chemical Science & Engineering, Faculty of Engineering, Kobe University, Rokkodai-cho, Nada, Kobe 657

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Titanium oxide thin film could be prepared from $(NH_4)_2TiF_6$ aqueous solution with addition of boric acid by Liquid Phase Deposition (LPD) process. The aspect and chemical composition of the deposited films were different according to the concentration range of $(NH_4)_2TiF_6$ and H_3BO_3 in the treatment solution. The deposition rate of transparent TiO_2 film increased with increasing concentration of added H_3BO_3.

Transition metal oxide thin films, which have various kinds of optical and electrical properties, are very widely used as inorganic functional materials in the fields of application. Generally, these metal oxide thin films were prepared by some dry processes such as sputtering and C. V. D. and some wet processes such as sol-gel method. Recently, a new wet process to prepare metal oxide thin films has been developed. This process is called Liquid Phase Deposition (LPD) process.[1] In this process, metal oxide thin films could be deposited on the immersed substrates by using chemical equilibrium reaction between the metal fluoro-complex ion and the metal oxide in the aqueous solution. This process is easy to apply to various kinds of substrates with large surface area and/or complex morphology without special equipment at room temperature. In the present letter, we report the preparation of titanium oxide thin films by using LPD process.

Hexafluorotitanate ammonium ($(NH_4)_2TiF_6$; Kishida Chemical Co. Ltd.) and boric acid (H_3BO_3; Nacalai Tesque Inc.) were dissolved in distilled water at the concentration of 0.5 mol/dm^3 (M). $(NH_4)_2TiF_6$ and H_3BO_3 solutions were mixed at various compositions and used as the treatment solution for deposition. Non-alkali glass (Corning, # 7059) was used as substrate. The substrate was degreased and washed ultrasonically, then the substrate was immersed into the treatment solution and kept suspended vertically. The temperature of the treatment solution was kept at 25 °C. After appropriate reaction time, the sample was took out from the treatment solution, washed with distilled water and dried at room temperature. Some of these samples were calcined at various temperature under air flow.

X-ray diffraction for the deposited films were measured with Rigaku RINT 2100 diffractometer, using Cu Kα radiation. IR absorption spectra of the deposited films were measured with IR spectrophotometer A-302 (Japan Spectroscopic Co. Ltd.). Thermogravimetric analysis (TG) for the deposited film which scratched out from the substrate was carried out in air by Rigaku TG 8120, at a heating rate of 10 °C. The surface morphology of the film was observed with scanning electron microscopy (SEM; Hitachi, S-2500). The film thickness for the deposited transparent films, which showed interference color, were derived from the visible spectra of the films by interference method.

After reaction for several tens of hours, hazy or transparent films were deposited on the substrates. These films showed excellent adherence to the substrate. According to the aspect of deposited film, the concentration range of $(NH_4)_2TiF_6$ and H_3BO_3 is classified into four groups (Figure 1). By X-ray diffraction measurements for the deposited films, it was found that the deposited film was hazy anatase at the region I, and that at the region II was transparent anatase. Fluorine was not detected by the qualitative analysis using $CaCl_2$ for the film deposited at the region II which dissolved in diluted HNO_3. Peak intensity of the diffraction of anatase for the film deposited at the region II were larger than that for the film deposited at the region I. The crystallite size for the film deposited at the region II, calculated by the Scherrer's equation for the (101) peak of the X-ray diffraction patter of anatase, was increased by the calcination from several nanometers for the as-deposited film to *ca.* 20 nm for the film calcined at 600 °C. For the calcined film at 600°C, no diffraction peaks except that of anatase were observed. At the region III, micro-crystalline of NH_4TiOF_3 was deposited on the substrate. At the region IV, any deposition was not recognized. When another substrates such as alumina ceramic plate or stainless steel were used, similar results were obtained.

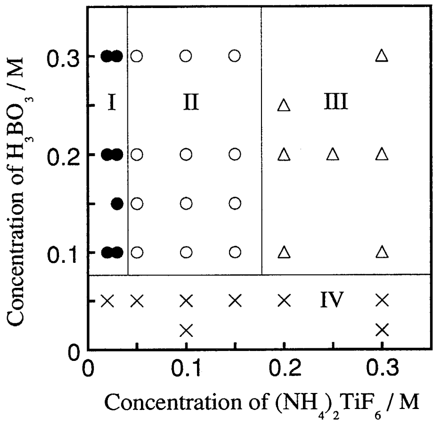

Figure 1. Relationship between aspect and chemical compositions of the deposited film and the concentration range of $(NH_4)_2TiF_6$ and H_3BO_3. ● ; hazy anatase, ○ ; transparent anatase, △ ; NH_4TiOF_3, × ; no deposition.

From the measurement of diffuse reflectance spectra of the deposited film at the region II, absorption edge of the as-deposited film was *ca.* 365 nm which is higher energy than the bulk anatase crystal, 388 nm. The absorption edge was shifted to the lower energy by the calcination.

In IR absorption spectrum of the deposited film, absorption bands at *ca.* 3200 cm^{-1}, 1620 cm^{-1} and 1400 cm^{-1} were observed. Absorption bands at 3200 cm^{-1} and 1620 cm^{-1} are assigned to an O-H stretching mode and H-O-H deformation mode, respectively. These bands are assigned to the physically and chemically adsorbed water molecules. Absorption band at 1400cm^{-1}

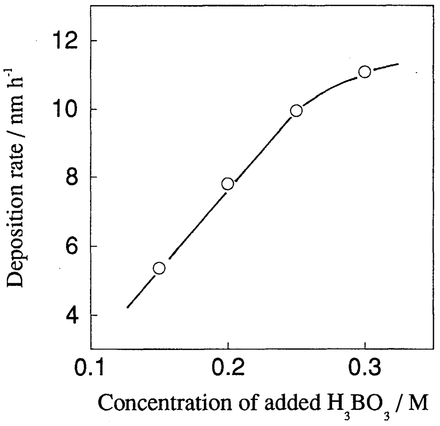

Figure 2. Relationship between the deposition rate and the concentration of added H_3BO_3.

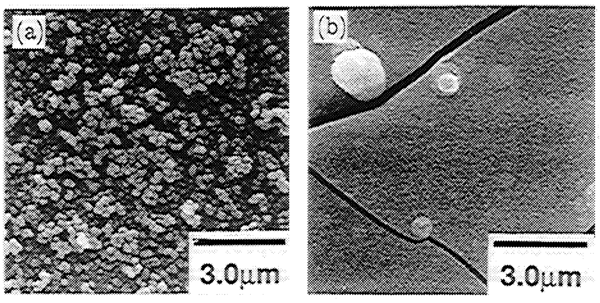

Figure 3. SEM photographs of the deposited films. (a); region I, (b); region II.

is assigned to N-H deformation mode of NH_4^+. NH_4^+ which were contained in $(NH_4)_2TiF_6$ which is one of the source materials for deposition, were enclosed in the deposited oxide film during the reaction. These bands disappeared by the calcination above 300 °C completely. From TG measurement of the deposited film, weight loss mainly due to elimination of water was about 20 wt%.

For the hydrolysis of $[TiF_6]^{2-}$ ion in aqueous solution, the following equilibrium scheme has been proposed by Schmitt *et al.*[2]

$$[TiF_6]^{2-} + nH_2O \rightleftharpoons [TiF_{6-n}(OH)_n]^{2-} + nHF \quad (1)$$

However, under the law of mass action, the equilibrium can be changed by the addition of H_3BO_3 as F^- scavenger into the solution. H_3BO_3 easily reacts with F^- ion and forms more stable complex as[3]

$$H_3BO_3 + 4HF \rightleftharpoons HBF_4 + 3H_2O. \quad (2)$$

The addition of H_3BO_3 leads to consumption of non-coordinated F^- ions and accelerates the hydrolysis reaction. From the results of X-ray diffraction, which showed the deposited film was TiO_2, it is considered that the deposition of TiO_2 thin film arose through the dehydration reaction among $[Ti(OH)_6]^{2-}$, which was generated by hydrolysis reaction of $[TIF_6]^{2-}$. In the region III, added H_3BO_3 was insufficient for the hydrolysis to be completed because concentration of $(NH_4)_2TiF_6$ is high; consequently, titanium oxy-fluoride was supersaturated and deposited onto the substrate. The film thickness of the film deposited at region II increased linearly with reaction time up to 80h. The deposition rate got to decrease with reaction time over 80h. It can be said that the decreasing of reactant concentration led to decreasing of the deposition rate. The deposited film was peeled off when reaction time was more than 130 h. The deposition rate of the film was depended on the concentration of added H_3BO_3 as F^-scavenger (Figure 2). The deposition rate increased linearly with concentration of H_3BO_3 up to 0.25 M. This indicates that rate-determining step of this reaction is F^- consuming reaction by H_3BO_3.

Figure 3 shows SEM photographs of the films which deposited at region I and II. The film was constructed of polycrystalline particles. Constructed particles of the film deposited at the region I are several hundreds of nanometers which scatter visible ray, thus, the film deposited at the region I was hazed. On the other hand, constructed particles of the film deposited at the region II are smaller than that of region I, which are smaller than the wavelength of visible ray; therefore, the film deposited at region II was transparent. Some cracks were also observed for the film deposited at the region II. It is considered that these cracks were generated by internal stress of the film due to contract of the film by dissociation of water on drying procedure.

The following results were obtained from the present study.
(1) Titanium oxide thin films were prepared on glass substrates by LPD method by using of hydrolysis reaction of $[TiF_6]^{2-}$ driven by the addition of H_3BO_3 as a F^- ion scavenger.
(2) The aspects and chemical compositions of the deposited films were different according to the concentration range of $(NH_4)_2TiF_6$ and H_3BO_3. At low concentration range of $(NH_4)_2TiF_6$, hazy or transparent anatase TiO_2 films were deposited. At high concentration range of $(NH_4)_2TiF_6$, thick films of micro-crystalline NH_4TiOF_3 were deposited.
(3) Thickness of the deposited TiO_2 film increased linearly with reaction time and the deposition rate of transparent TiO_2 film depended on the concentration of added H_3BO_3.

References

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