

PREPARATION OF HETERO-STRUCTURED OXIDE THIN FILMS BY THE LIQUID-PHASE DEPOSITION (LPD)

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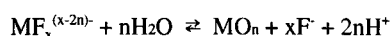
New preparation method for thin metal oxide films with hetero-structure was developed by applying of the Liquid-Phase Deposition, LPD, method. The Liquid-Phase Deposition method is one of wet processes for preparing metal oxide thin films from aqueous solution. In this process, by the addition of F⁻ ion scavenger, the chemical equilibrium between metal fluoro-complex and metal oxide was shifted and homogeneous metal thin film deposited on the various kind of substrates. And also, some composite film could be obtained easily by this method. In this paper, we report on the preparation of hetero-structured oxide thin films which contained various kinds of hetero-phases such as nano-sized metal particles in the film or multi-layered film.

Key words: metal oxide, thin film, hetero-structure, liquid-phase deposition

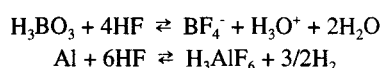
1. INTRODUCTION

Metal oxide thin films have been prepared by some kinds of gas phase processes, such as sputtering, CVD, vacuum evaporation, laser ablation, and so on. Those methods are applied to the thin film formation techniques for various kinds of metal oxides and used widely in industrial fields. However, these processes have several problems. For instance, they are not suitable for the preparation of thin films on substrates with large surface area or complex surface morphology, and also require some advanced special apparatuses, such as vacuum system, high power laser, microwave generator and so on, for deposition of films.

A novel wet process, which overcomes some of those problems, had been developed. This process is called Liquid-Phase Deposition, LPD, method [1,2]. The LPD method is unique wet process for the formation of metal oxide thin films. This process utilizes ligand-exchange, hydrolysis, equilibrium reaction of metal-fluoro complex species, MF_x^{(x-2n)-}, and F⁻ consumptive reaction. In aqueous solution, MF_x^{(x-2n)-} is hydrolysed with water following ligand-exchange equilibrium reaction:



This equilibrium reaction is shifted to the right-hand side by the F⁻ consumptive reaction with boric acid, H₃BO₃, or aluminum metal as a F⁻ scavenger, which readily reacts with F⁻ and form stable complex as follows:



The addition of the F⁻ scavenger leads to consumption of free F⁻ ions, and accelerates the ligand-exchange reaction. By using this method, metal oxide or hydroxide thin films can be formed on the substrates which are immersed into the solution by very simple procedure, and it does not require any special equipment and high energy. As the LPD method is performed in aqueous solution system, thin films formed all over the

surface of the substrates with large surface area and complex morphology. So far, we have already developed and reported the preparation of various kinds of metal oxide thin films such as titanium oxide [3], vanadium oxide [4,5], iron oxide [6], and so on [7,8] by the LPD method.

In this paper, we applied to the LPD method to the preparation of hetero-structured oxide thin films such as metal particles dispersed oxide and multi-layered oxide thin films.

2. EXPERIMENTAL

2.1 Metal particles dispersed oxide thin films

As parent solutions, ammonium hexafluorotitanate, (NH₄)₂TiF₆, and boric acid, H₃BO₃, were dissolved in distilled water at concentrations of 0.5 mol dm⁻³. For deposition of Ag/TiO₂ system, AgNO₃ aqueous solution was used as Ag source, and for Pt/TiO₂ system, Pt(NH₃)₄Cl₂ aqueous solution was used for Pt source. These solutions were mixed with various concentrations and used as the treatment solution for deposition. The films were deposited at a concentration of 0.10 mol dm⁻³ for (NH₄)₂TiF₆ and of 0.20 mol dm⁻³ for H₃BO₃. This solution composition is that corresponding to the concentration at which the transparent anatase thin film was formed [3]. As the substrate, non-alkali glass, Corning #7059, was used. After being degreased and washed ultrasonically, the substrate was immersed in the treatment solution and suspended therein vertically for several hours. Heat treatment was performed under nitrogen flow for Ag/TiO₂ system and in air flow for Pt/TiO₂ system for 1 h at various temperatures from 100 to 600 °C.

2.2 Multi-layered oxide thin films

Multi-layered thin films of titanium oxide and iron oxide were prepared by the LPD method. Alternative deposition of titanium oxide and iron oxide was used to fabricate multi-layer. As parent solutions for deposition of titanium oxide, (NH₄)₂TiF₆ aqueous solution was used. And for iron oxide, FeOOH-NH₄F-HF aqueous solution were used. From this treatment solution, crystalline β-FeOOH thin films are formed, and they transform to α-Fe₂O₃ by subsequent

heat-treatment [6]. H_3BO_3 aqueous solution was used as F⁻ scavenger. Deposition process was similar to the Section 2.1.

2.3 Characterization of the deposited films.

Composition analyses of the deposited films were carried out by ICP atomic emission spectrometry, Seiko Instruments Inc., SRS 1500 VR, for the solutions produced by dissolving the films with diluted hydrochloric acid solution. X-ray diffraction measurements were carried out with a Rigaku RINT-2100 diffractometer with thin film attachment, using Cu-K α radiation. The measurements were made at 1° of x-ray incident angle. XPS analyses were carried out by KRATOS, XSAM 800 with Mg-K α radiation (1253.6 eV). Obtained spectra were corrected by referring to contamination C 1s line (284.6 eV). TEM was performed by a JEOL, JEM 2010 with an acceleration voltage of 200 kV.

3. RESULTS AND DISCUSSION

3.1 Formation of metal particles dispersed thin film

3.1.1 Ag/TiO₂ system

Figure 1 shows the relationship between the concentration of AgNO_3 in the treatment solution and the Ag/Ti atomic ratio of the deposited films. The Ag content increased up to 0.087 with an increased of the AgNO_3 concentration. In order to investigate the chemical state of Ag in the film, XPS were measured. Figure 2 shows Ag 3d electron spectra of as-deposited film and films heat treated at various temperatures. For as-deposited film, peak binding energy of Ag 3d_{5/2} was observed at 367.4 eV which accord with Ag^+ [9], indicating that silver species were existed as Ag^+ ionic species in the as-deposited film. The observed Ag 3d peak was shifted to lower energy side with increasing heat treatment temperature. For the films heat-treated at 200 to 500 °C, Ag 3d_{5/2} peak was 368.0 eV which accorded with that of metal Ag [9]. It was confirmed that Ag^+ in the as-deposited film was reduced to metal Ag by the heat treatment. On the other hand, Ag 3d peaks were weakened and shifted toward lower energy side for the film heat-treated at 600 °C. Peak binding energy of Ag 3d_{5/2} of the film heat-treated at 600 °C was 367.7 eV which accorded with that of Ag^+ , suggesting that metal Ag was again oxidized to Ag^+ with oxygen in the film.

Micro-structure of the films were observed by TEM and selected area electron diffraction (SAED). Figure 3 show TEM images of films heat treated at various temperatures. Although particles were not observed for the as-deposited film, several particles were observed for the film heat-treated at 300 and 500 °C. It indicates that Ag^+ ionic species in the as-deposited film reduced to Ag metal by the heat-treatment under nitrogen flow. It is well agreed with the XPS data. From SAED pattern of the film heat-treated at 500 °C, diffraction spots assigned to Ag metal were observed. The dispersed Ag metal particles were spherical and growing up of the particles with increasing heat-treatment temperature was observed.

3.1.2 Pt/TiO₂ system

The relationship between Pt/Ti atomic ratio of

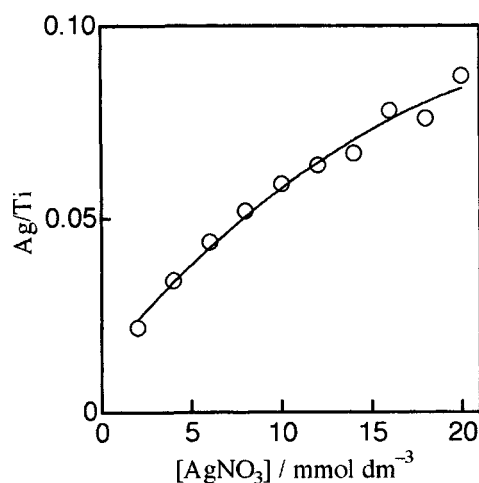


Fig. 1. Relationship between Ag/Ti atomic ratio of films and concentration of AgNO_3 in the treatment solution.

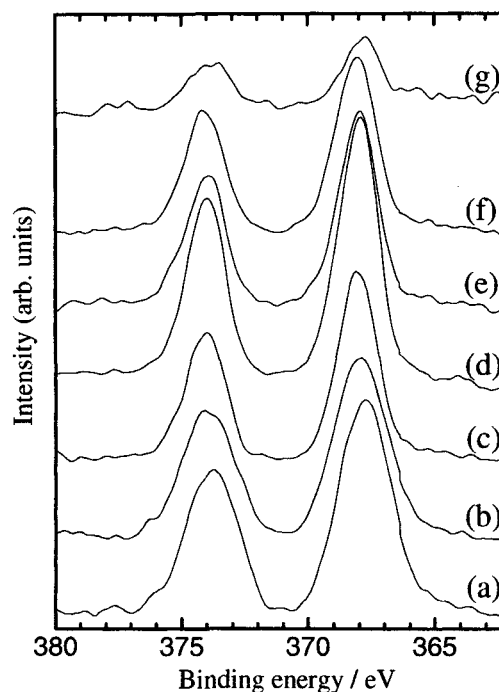


Fig. 2. Ag 3d electron spectra of films heat-treated at various temperatures. (a); As-deposited film, (b) to (g); films heat-treated at 100, 200, 300, 400, 500, and 600 °C.

the formed films and the concentration of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ in the treatment solution is shown in Fig. 4. Similar in case of Ag/TiO_2 system, Pt content of the deposited film increased with increasing the concentration of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$.

Chemical state of the incorporated Pt was

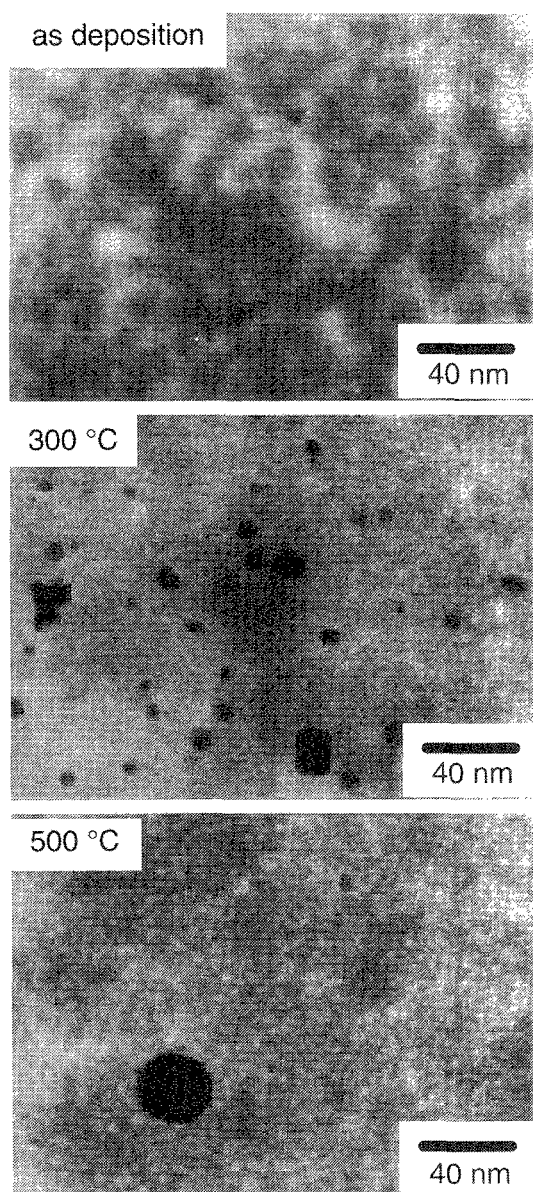


Fig. 3. TEM images of the deposited films heat-treated at various temperatures.

observed by XPS. For the as-deposited film, the Pt $4f_{7/2}$ peak was separated into 72.9 and 74.2 eV, which are assigned to Pt^{II} and Pt^{IV}, respectively [10]. It indicates that the Pt was incorporated in a titanium oxide matrix as an ionic species in as-deposited film, and Pt^{II} was partially oxidized to Pt^{IV} in the process of the film formation. The spectra of films after heat-treatment at 200 and 300 °C were broadened, and lower energy component positioned at 70.5 eV was observed. This component was assigned to Pt metal. The Pt 4f peak was sharpened and shifted to the lower energy side for the film heat-treated at 600 °C. The peak position of Pt $4f_{7/2}$ was observed at 70.3 eV which was closer to that of Pt metal, although the existence of oxidized platinum species was observed a little in the curve-fitted spectrum.

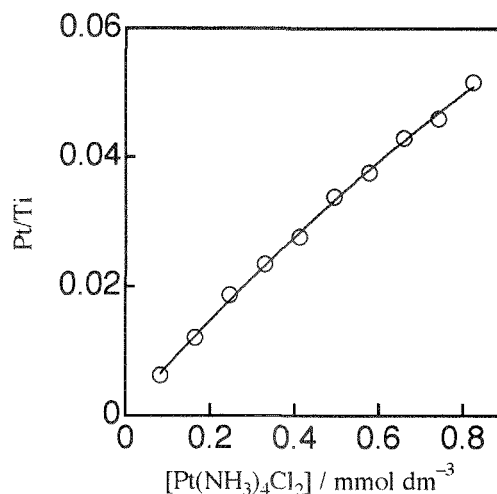


Fig. 4. Relationship between Pt/Ti atomic ratio of films and concentration of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ in the treatment solution.

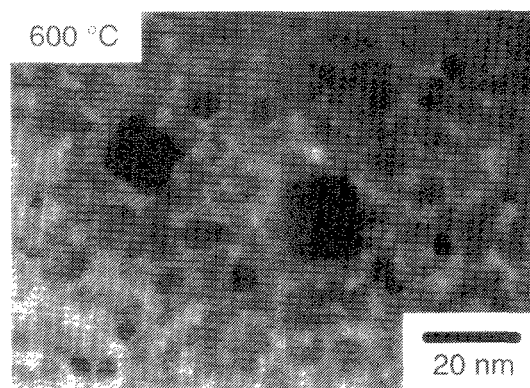


Fig. 5. TEM image of the deposited film heat-treated at 600 °C.

TEM images of the films are shown in Fig. 5. In the as-deposited film, metal particles were not observed in TEM image. TEM image of film heat-treated at 600 °C showed nano-sized particle of Pt dispersed in the titanium oxide thin film. SAED patterns of the film heat-treated at 600 °C showed clear spots assigned to crystalline Pt metal.

3.2 Formation of multi-layered thin films

Multi-layered thin films consisted of TiO_2 and $\beta\text{-FeOOH}$ or $\alpha\text{-Fe}_2\text{O}_3$ were prepared. Bi-layered and tri-layered thin films could be obtained by the alternative deposition by sequential dipping into the treatment solutions.

Figure 6 shows XPS depth profiles of formed $\text{TiO}_2/\beta\text{-FeOOH}$ bi-layered thin films. From these profiles, it is confirmed that the boundary among those layers was definite with the composition and the crystallography. The depth profiles of the bi-layered

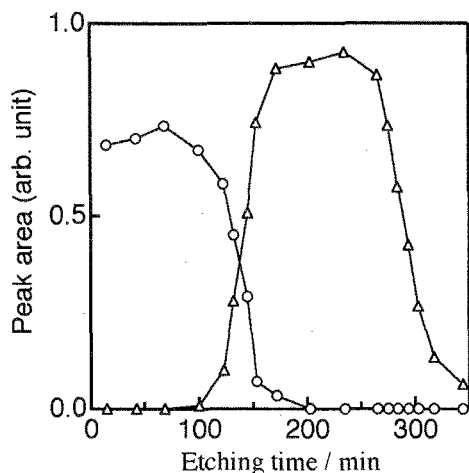


Fig. 6. XPS depth profiles of $\text{TiO}_2/\beta\text{-FeOOH}$ bi-layered film. \circ ; Ti, \triangle ; Fe.

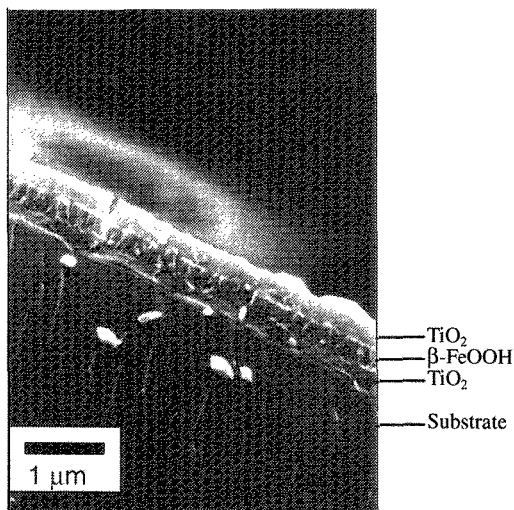


Fig. 7. Cross-sectional SEM image of $\text{TiO}_2/\beta\text{-FeOOH}/\text{TiO}_2$ tri-layered film.

film after heat-treatment at $400\text{ }^\circ\text{C}$ showed that annealing caused interdiffusion of the elements at the interface, and gradual changes in content of iron and titanium through the interface was observed.

The cross-sectional SEM image of $\text{TiO}_2/\beta\text{-FeOOH}/\text{TiO}_2$ tri-layered thin film is shown in Fig. 7. The interface between TiO_2 and $\beta\text{-FeOOH}$ was clearly observed, and exfoliation of each film was not observed. It can be possible to form more-layered structure and more component multi-layer thin films by repeating the LPD process.

4. CONCLUSIONS

We have developed a very simple process for the preparation of hetero-structured oxide thin films by the LPD method. In this paper, two types of hetero-structured oxide thin films were prepared. One is the nano-sized metal particle dispersed oxide thin films and the other is multi-layered oxide thin films.

TiO_2 thin films containing Ag and Pt nano-sized metal particles were formed by the LPD method from mixed solution of $(\text{NH}_4)_2\text{TiF}_6$ and H_3BO_3 with addition of aqueous solution containing objective noble metal ions, such as AgNO_3 and $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$. The Ag and Pt contents in the films were controlled easily by controlling the concentrations of objective metal ions in the treatment solution. As-deposited state, added metals were existed as ionic species, and were reduced to metal by the heat-treatment and produced dispersed metal particles. The size of the dispersed metal particles was increased with increasing heat treatment temperature.

Multi-layered oxide thin films were formed by the alternative deposition by sequential LPD process. In this paper, two components, titanium oxide and iron oxide, multi-layered thin films were prepared. The boundary among each layer was definite and clearly observed by SEM. After the heat-treatment, interdiffusion of the elements at the interface and gradual changes in content of iron and titanium through the interface were observed.

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