Control of Composition Gradient in Functionally Graded Ti/Fe Oxide Film Prepared by the Liquid Phase Deposition Method

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The Fe/Ti oxide films with composition gradient were prepared from metal fluoro-complex aqueous solutions by the Liquid Phase Deposition (LPD) method. Gradient composition of the Fe/Ti graded oxide thin films were investigated by using a cross-sectional TEM, EDX microanalysis and FE-SEM. The composition gradients of the deposited films in the direction of the film growth were controlled by changing the mixed conditions of the reacting solution. The Ti/Fe oxide films in which the direction of composition gradient was changed reversely for Fe/Ti graded thin films, were also successfully prepared. The effect of heat treatment on the changes in the microstructure of the films was investigated by using by HRTEM and XRD. After heat treatment under air flow, the crystalline TiO₂ was increased compared with that in the as-deposited film, and the transformation into α -Fe₂O₃ from β -FeOOH were observed near the top-surface of the film and the substrate, respectively.

Key Words: Liquid Phase Deposition, Functionally graded materials, metal oxide, thin film

1. INTRODUCTION

A functionally graded materials (FGMs) are one in which the composition and/or the microstructure vary in the direction of the film thickness [1-3]. FGMs are of particular practical interest because the physical and chemical properties are varied in the direction of thickness. For such materials, various kinds of fabrication methods were employed, using chemical and physical techniques [4-7]. Since FGMs properties strongly are depend on the composition and microstructure, it is important to develop the fabrication methods that provide the desired characterizations in FGM. The thin films with composition gradient might be suitable for a variety of optical fiber application and solar cells [8-10]. However, these thin films with composition gradient prepared by the conventional technique have stepwise structures which are characterized by abrupt changes in composition arising from the limitations of the manufacturing route. A facile technique is thus desirable for the preparation of thin films with continuous gradient in the direction of the film thickness.

We have previously developed the Liquid Phase Deposition (LPD) method as a new fabrication process for preparing metal oxide thin films.[11-13]. In this process, metal oxide thin films are formed by means of the ligand exchange equilibrium (hydrolysis), reaction of metal-fluoro complex species, $MF_x^{(x,2n)}$, and F consumptive reaction by boric acid or aluminum metal as F scavenger. By using this technique, we have previously developed the preparation of the Si/Ti graded oxide thin film [14]. We have shown that the composition gradient of the Si/Ti oxide film in the direction of the film growth can be prepared by changing the operating conditions. In this study, we attempted to elucidate gradient control in the direction of Fe/Ti oxide film growth by controlling the treatment solution. The thin films with composition gradient were prepared to investigate the effect of concentration of the treatment solution. The characteristics of microstructure and composition of deposited film are investigated by using a cross-sectional TEM equipped with an X-ray microanalyzer and FE-SEM. The effect of the heat-treatment on the changes in the microstructure of the films was also investigated by XRD and HRTEM analyses.

2. EXPERIMENTAL

In the present study, Fe/Ti graded oxide films were prepared by the LPD method, from (NH₄)₂TiF₆, H₃BO₃ and FeOOH-NH4F HF aqueous solutions. Borosilicate glass and Au wire were used as the substrate, degreased and washed ultrasonically prior to use. For the deposition of Fe/Ti graded oxide thin films, as a first time, the substrates were immersed into the solution kept at 30°C, containing metal-fluoro complex and H₃BO₃ (solution A). After standing for several hours (this time is denoted as pre-treatment time), the solution which contained another metal-fluoro complex and H₃BO₃ (solution B) was added to solution A, and the mixed solution was removed simultaneously in order to maintain the volume of the treatment solution (250 ml) at constant flow rate. The addition and subtraction rates were controlled by a fixed flow console pump. After addition of Solution B for several hours (this time is denoted as dropping time), the substrates with deposited films were removed from the solution, washed with distilled water and dried at room temperature. Table I shows the composition of the parent solution and operating conditions applied to the present work. In the present study, in order to confirm the effect of the concentration of the treatment solution, the graded films were prepared under various kinds concentration of the solution A and B. Three series of samples were prepared. Samples in series A were prepared at various kinds concentration of FeOOH-NH4F HF in the solution A. Samples in series B were prepared at various kinds concentration of (NH₄)₂TiF₆ and FeOOH-NH4F in the Solution A. Samples in series A and B were the graded films in which Ti fraction increased in the direction of the film growth (these series is denoted as Fe/Ti system). Sample in series C were prepared by changing the

	Series A			Series B			Series C
Sample	1	2	3	4	5	6	7
$\label{eq:solution} \begin{array}{l} \hline Solution \ A \\ FeOOH \cdot NH_4 F \cdot HF \ / \ mmol \ dm^{-3} \\ (NH_4)_2 Ti F_6 \ / \ mol \ dm^{-3} \\ H_3 BO_3 \ / \ mol \ dm^{-3} \end{array}$	2.0 0.20	5.0 	8.0 	2.0 0.060 0.20	3.0 0.040 0.20	4.0 0.020 0.20	0.10 0.20
Pre-treatment time / hour Flow rate / ml min ⁻¹	2.0 0.40	2.0 0.40	2.0 0.40	20 0.40	20 0.40	20 0.40	7.0 1.5
Solution B FeOOH•NH4F•HF / mmol dm ⁻³ (NH4)2TiF6/ mol dm ⁻³ H3BO3 / mol dm ⁻³	 0.10 0.20	 0.10 0.20	 0.10 0.20	 0.10 0.20	0.10 0.20	0.10 0.20	5.0 0.20
Dropping time / hour Total reaction time / hour	20 22	20 22	20 22	20 40	20 40	20 40	11 18

Table I Preparation conditions of Ti/Fe graded films.

Ti and Fe species of solution A and B reversely, respectively. Sample in series C were the graded film in which Ti fraction decreased in the direction of the film growth (this series is denoted as Ti/Fe system) for comparison with samples in series A and B. Heat treatments of the deposited films were carried out in air flow for 1 h at 500°C.

The microstructure and composition of the deposited films were identified by using a cross-sectional transmission electron microscope (TEM, JEOL JEM-2010) equipped with an EDX microanalyzer (NORAN Instrument, Inc.) operating at 200 kV, which provided a 0.19 nm point resolution. The difference in the composition of the films in the direction of the film growth was discriminated by X-ray microanalysis using 5 nm electron probe. Thin cross sections with a thickness of ca. 25 nm were obtained with a Leica Ultracut UCT ultramicrotome using a diamond knife. Surface morphology of deposited thin films was observed by a field emission scanning electron microscope (FE-SEM; JEOL JSM-6335F). The structure of deposited thin films was analyzed by using X-ray diffractometry (XRD; RINT-TTR, Rigaku Co.Ltd.) using Cu-Ka radiation (300 kV, 50 mA).

3. RESULTS AND DISCUSSION

We investigated influence of initial concentration of FeOOH-NH₄F·HF in solution A on the composition gradient of deposited films (Series A). In Fig. 1, the molar fractions of Fe and Ti, determined by quantitative analysis, are plotted as

a function of the direction of film thickness toward the top surface, respectively. The films with various depth profiles and thicknesses were prepared. For the sample 1 prepared at lowest concentration of [Fe³⁺] [2 mmol dm⁻³, Fig. 1(a)], the Fe fraction abruptly decreases from 1.0 to 0 over the range 0-360 nm in a fashion that parallels the corresponding increase in the Ti fraction from 0 to 1.0. Only TiO₂ was deposited between 150 to 360 nm from the substrate. Fig. 1 (b)-(c) shows the depth profile under different initial concentration of $[Fe^{3+}]$. For sample 2 and 3, the Ti fraction increases from 0 to 1.0 over the range of 0-200 nm [Fig. 1 (b)] and from 0 to 0.5 over the range of 0-340 nm [Fig. 1 (c)]. The depth profiles gradually changed with increasing of initial concentration of $[Fe^{3+}]$. The increase of the initial concentration of $[Fe^{3+}]$ in solution A directly lead to a time dependent change in the concentration of Ti and Fe species in the treatment solution during film deposition. Because the sample 3 was prepared at highest concentration of [Fe³⁺] employed, the change in the concentration of Ti and Fe species in the treatment solution was slowly. Therefore, the graded films obtained, of which the Fe content is much higher close to the substrate for sample 3. It can be observed that initial concentration of solution A affects significantly the depth profile of the deposited films.

The results of EDX measurement shows that the film thicknesses of the graded films were changed at various reaction conditions. In addition, it was found that the composition of all the graded film changed non-linearly in



Fig. 1 Depth profiles of Ti and Fe atomic fraction in the deposited films prepared with different initial concentration of [FeOOH-NH₄F·HF] (Series A). (a)-(c): film deposited for 2, 5 and 8 mmol dm⁻³.





the direction of the film thickness. These results are considered to be due to the difference of deposition rates at the composition of the treatment solution.

Above these results, the preparation of the Fe/Ti graded oxide film with various depth profiles was successful by the LPD method. However, only Fe/Ti oxide films of which the Fe content was higher neat the substrate were obtained. Therefore, the second attempt was made with the graded films which were prepared by changing the compositions of initial concentration of solution A in order to change the composition near the substrate (Series B). The films with various depth profiles were prepared in Fig. 2 (a)-(c). Ti fractions near the substrate of graded films were changed from 0.3 to 0.8 with increasing initial concentration of [Fe³ (and decreasing initial concentration of [T14+]). From Fig. 2 (a)-(c), the Ti fraction near the substrate was successfully controlled over a wide range by this technique. Such thin films may be useful for solid state solar cells and optical filters.

However, only Fe/Ti oxide films of which the Ti content was higher close to the top of the surface were obtained. Therefore we attempted to prepare the Ti/Fe graded films (Series C). Fig. 2 (d) shows the depth profiles of Ti/Fe system. It was confirmed that direction of composition gradient changed reversely for Fe and Ti graded thin films. Contrary to Series A, the Ti fraction decreased from 1.0 to 0 in the direction of the film growth for Series B.

Fig. 3 (a)-(b) shows FE-SEM images for the graded films



Fig. 3 SEM photographs of the graded films. : films deposited for (a) Fe/Ti graded film (sample 2) and (b): Ti/Fe graded film (sample 5).

for sample 2 (Fe/Ti system) and sample 7 (Ti/Fe system), respectively. For the all films, no cracks were observed. For sample 2 [Fig. 3 (a)], the deposited film was constructed of grains of 350 nm in dimension. The constructed grains of the film deposited for sample 7 [Fig. 3. (b)] was consisted grains of 20 nm in dimension. In the previous study, the grains of titanium oxide films were less than 20 nm and that of β -FeOOH films were as large as several hundreds of nanometers [15]. In addition, when multi-layered thin films consisted of TiO₂ (over layer) and β -FeOOH (under layer), were prepared, the multi-layered thin film was similar as the grains size of β -FeOOH [16]. Above these results, the grains size of the thin films with composition gradient was also influenced by the grains size of underlayer (TiO₂ or β -FeOOH).

In order to clarify the observed effect of heat treatment, the microstructure of film was investigated. Fig. 4 (a) shows the cross-sectional TEM image of the graded film of sample 2. The substrate used is Au wire which corresponds to the dark region seen at left-hand side in Fig. 4 (a). It confirms that no cracks in films and no peel-off of the films were



Fig. 4 Cross-sectional TEM images of Fe/Ti graded films after heat-treatment at 500° C. (a): the graded film prepared for sample 2. (b)-(c) : HR-TEM image of Fe/Ti graded film near the Au substrate (point A) and top-surface of film (point B).



Fig. 5 XRD patterns for graded oxide thin films for Fe/Ti graded oxide thin film (sample 2). (a): as-deposition (b): after heat-treatment at 500°C.

observed. Theses results are considered to be due to the feature of FGMs. In FGMs, the residual thermal stress caused by the difference in coefficient of thermal expansion was relaxed to some extent due to gradual composition in nanometer scale [17].

No changes of the depth profiles and thickness of the films heat treated at 500°C were observed from that of the as-deposited film. It is indicated that Fe and Ti ions could not be diffused into the film. Fig. 4 (b) and (c) shows high-resolution TEM (HRTEM) images near the substrate and surface of films, respectively, [the point A and B in Fig. 4 (a)]. At the point of A and B, lattice fringes corresponding to α -Fe₂O₃ (104) plane and *anatase*-TiO₂ (101) plane were clearly observed near the substrate and the top-surface, respectively, indicating that α -Fe₂O₃ and TiO₂ are crystalline. However, the number of crystalline of TiO₂ phase decreased with decreasing the Ti fraction in the range 1.0 to 0.9. In the Ti fraction range of 0.20-0.90, the crystalline α -Fe₂O₃ and TiO2 were not observed and the film was mostly amorphous. Fe_xTiO_y phase was not formed in this sample. This implies that phase formation does not occur because calcination temperature was much lower (500°C) than required by the formation of FexTiOy phase. Ishikawa and Inouye [18]-[19] reported that .- FeOOH is transformed into crystalline α-Fe₂O₃ above 400 °C and Pal et al. [20] reported that Fe2TiO5 phase started forming at 700°C.

Fig. 5 shows XRD patterns for as-deposited film and film heat treated at 500°C. XRD pattern of deposited film showed some diffraction peaks which were assigned to β -FeOOH,. On heat treatment under flowing air, the microstructure of the graded film was changed significantly in the depth direction. The diffraction peaks of the graded film heat-treated at 500°C are assigned to α -Fe₂O₃ and TiO₂. In this study, these results are consistent with the TEM observation. It was confirmed that the as-deposited film with composition gradient has microcrystalline β -FeOOH and nanocrystalline *anatase* TiO₂ near the substrate and the top-surface. These results of XRD analysis demonstrates that crystallinity of TiO₂ in the graded film was increased and . -FeOOH was transformed into α -Fe₂O₃ by heat treatment.

4. CONCLUSIONS

The Fe/Ti oxide thin films with various gradient compositions have been prepared by the LPD method. From TEM observation and EDX measurement, it was elucidated that the composition gradients of the deposited films in the

direction of the film growth were controlled by changing the mixing conditions of the reacting solution. The Ti/Fe oxide film was also successfully prepared by changing the Ti and Fe species of solution reversely. After heat treatment in air flow, crystallinity of TiO₂ increased compared with that of the as-deposited film, and the transformation into α -Fe₂O₃ from β -FeOOH was observed near the substrate and the top-surface, respectively. The number of crystalline α -Fe₂O₃ decreased along the film thickness toward the top-surface. α -Fe₂O₃ and *anatase* TiO₂ plane were not observed in the Ti fraction range 0.20–0.90 and Fe_xTiO_y phase was not formed.

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