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The Effect of EDTA and EDTA Rare Earth Metal Complex on TiO_2 Film Deposition by the Liquid Phase Deposition (LPD) Method

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We have investigated the effect of addition of EDTA and *Ln*(EDTA)$^{n+}$ (EDTA rare earth metal complex) on TiO_2 film deposition by the liquid phase deposition (LPD) method. The film prepared from the precursor solution without EDTA showed flat texture, while the films via the precursor solution with EDTA and *Ln*(EDTA)$^{n+}$ were made of many nano-particles with ca. 500 nm in diameter. The amount of the TiO_2 film deposited on glass substrate was decreased with increasing the initial concentration of EDTA in the precursor solution. From field-emission scanning electron microscope (FE-SEM) observation and FT-IR measurement, it was found that the addition of EDTA in the precursor solution hindered nucleation on glass substrate due to the adsorption of EDTA on the deposited TiO_2. Consequently, the difference of the nucleation density on the substrate causes the difference of the surface morphology for the films prepared from the precursor solution with/without EDTA.

Key words: liquid phase deposition, TiO_2, EDTA, *Ln*-EDTA complex, adsorption

1. INTRODUCTION

Rare-earth doped metal oxide thin films have attracted much attention because of their electrical [1-3], optical [4,5] and crystallographic [6] properties. Sol-gel [7,8], chemical vapor deposition [9], sputtering [10,11] and ion implanted [12] techniques have been considered so far as candidates for the preparation of uniform *Ln*/metal oxide thin films. To reduce energy consumption, it would be a great advantage if uniform *Ln*/metal oxide thin films could be fabricated at room temperature employing simple process.

We have developed and reported [13-17] a novel process to prepare metal oxide thin films from aqueous solution by the liquid phase deposition (LPD) method. Since this technique relies on the chemical equilibrium reaction between metal-fluoro complex and metal oxide under controlling of the mass-action law, homogeneous thin films can be deposited on the various kinds of substrates with large surface areas and complex morphologies. In addition, since this method is performed in a liquid phase, which is a typically homogeneous mixing system, it is easy to fabricate multi-component oxide thin films via one step process.

In this method, the following equilibrium reaction is presumed.

$$MF_x^{(x-2n)-} + H_2O \Leftrightarrow MO_x + HF \quad (1)$$

$$H_3BO_3 + 4HF \Leftrightarrow BF_4^- + H_3O^+ + 2H_2O \quad (2a)$$
$$Al + 6HF \Leftrightarrow H_3AlF_6 + 3/2H_2 \quad (2b)$$

By the addition of boric acid or aluminum metal which readily reacts with F^- ions and form more stable complex ions, the equilibrium reaction (1) shifts to the right-hand side (Eqs. (2a) and (2b)).

Recently, we have succeeded in the preparation of metal oxide thin films containing rare-earth elements using this method. Generally, rare-earth ions react with F^- ions rapidly and form insoluble LnF_3[18]. In our study, we used EDTA as a masking reagent for Ln^{3+} ions to prevent from forming LnF_3 precipitation in the reaction solution. However, the information of the detailed effect of complexon, such as EDTA and *Ln*(EDTA)$^{n+}$, on the film deposition is not sufficient.

In this paper, we report on the effect of EDTA and *Ln*(EDTA)$^{n+}$ on TiO_2 film deposition by the LPD method.

2. EXPERIMENTAL

The precursor solutions were prepared by dissolving ammonium hexafluorotitanate, $(NH_4)_2TiF_6$, and boric acid, H_3BO_3, in ion-exchanged water to give concentrations of 0.5 mol dm^{-3}. As parent solutions, ethylenediaminetetraacetic acid, H_2Na_2EDTA, was dissolved into distilled water, of which concentration was 0.1 mol dm^{-3}, and $Gd_2O_3$was dissolved into 10 % hydrochloric acid solution. Ammonium hydroxide (NH_4OH) was used to adjust pH of EDTA and $GdCl_3$ solutions to approximately 5.0. These solutions were mixed with various concentrations and used as the treatment solution. After preparing of the treatment solution, the concentration was 0.1 mol dm^{-3} for $(NH_4)_2TiF_6$ and 0.2 mol dm^{-3} for H_3BO_3. The concentration of EDTA and Gd-EDTA complex in the treatment solution was varied. Soda-lime glass and Si (111) wafer were used as substrates, after cleaning ultrasonically. Substrates were immersed into the treatment solution with different reaction times. The temperature of treatment solution was kept at 30 °C. After immersion for several hours, the substrates were

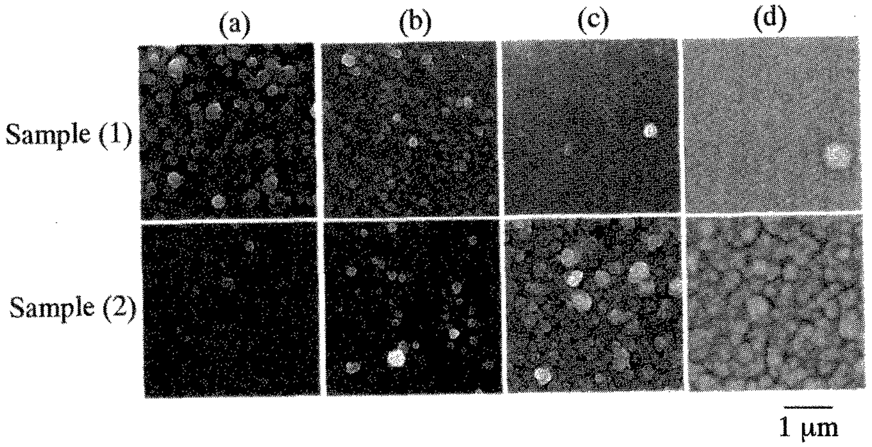

Fig. 1 SEM images of the deposited thin films with various EDTA concentrations [sample (1) 0 mM, (2) 2mM] and reaction times [(a) 2 hours (b) 9 hours (c) 15 hours (d) 24 hours].

removed from the reaction solution, washed with distilled water and dried at room temperature.

Composition analysis of the deposited films was carried out by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES: Seiko Instruments Inc., SRS 1500VR) for the solutions prepared by dissolving the films with diluted hydrochloric acid. The changes in the surface morphology of the deposited thin films with deposition time were observed using a FESEM (Jeol JEM 6335F). To investigate the chemical state of EDTA in the deposited thin film, fourier transform infrared (FT-IR) measurement was carried out. FT-IR spectrum was measured by refraction-absorption configuration using FT-IR instrument (FT/IR 615R, Japan Spectroscopic Co.) equipped with an MCT detector. The incident angle was set at 60°, and the light was set to the p polarization with a wire grid polarizer, which was arranged just before the specimen. The spectrum was recorded in a range of 1000-1800 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1 EDTA system

Figure 1 shows SEM images of the deposited films with various EDTA concentrations [sample (1) 0 mM, (2) 2 mM] and reaction times [(a) 2 hours, (b) 9 hours, (c) 15 hours, (d) 24 hours]. After the reaction for 2 hours (Fig. 1a), several small particles (i.e., nucleation) on the glass substrate can be observed. We note here that, in the SEM image for the sample (1), many particles can clearly be seen; on the other hand, for the sample (2), these particles can hardly be observed. After the reaction for 9 hours (Fig. 1b), the sample (1) consists of homogeneous and uniform clusters in the size of 200-300 nm. The formation of these clusters can be considered the result of the growth of particles in all three directions (i.e., nuclear growth). For the sample (2), such growth of the particles can not be seen, although the number of particles increased. The number of particles of the sample (2) reacted for 9 hours, however, were less than that of sample (1) reacted for 2 hours. This difference indicates the addition of EDTA in the treatment solution causes the depression of nucleation on the substrate and thus the nucleation density of the resultant sample becomes low. After the reaction for 15 hours (Fig. 1c), the thin film made of small particles can be observed for the sample (1). In contrast, the thin film in sample (2) made by many large clusters can be observed. After the reaction for 24 hours (Fig. 1d), the sample (1) forms dense and continuous thin film. For the sample (2), the formation of the thin film which has much grain boundaries resulting from the growth of particles can be observed. From this result, we consider the addition of EDTA into the precursor solution causes the depression of nucleation on the substrate and the difference in the observed surface microstructure for the TiO_2 samples originates from the nucleation density.

Figure 2 shows reaction time dependence of the deposited mass of Ti on the substrate. The remarkable increase of the deposited film mass on glass substrate was observed (after reacted for 3 hours and 9 hours for 0 mM and 2 mM-EDTA/TiO_2 film, respectively). The initial stage of the deposition, we call 'the induction period [19]', becomes long with increasing the initial concentration of added EDTA, whereas in the following stage of the deposited reaction, the film formation rates of the films prepared from precursor solutions with the addition of 0 mM and 2 mM EDTA were almost constant. From these results, it is concluded that the addition of EDTA in the precursor solution affects the induction period.

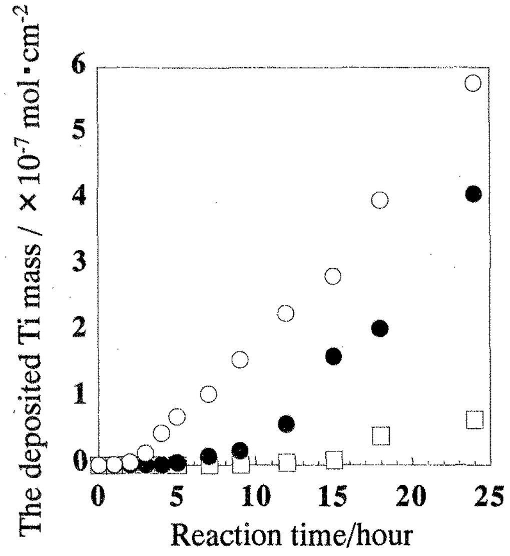

Fig. 2 Reaction time dependence of the deposited Ti mass on the glass substrate. The films prepared from the solution containing (○) 0 mM, (●) 2 mM, (□) 4 mM EDTA solution.

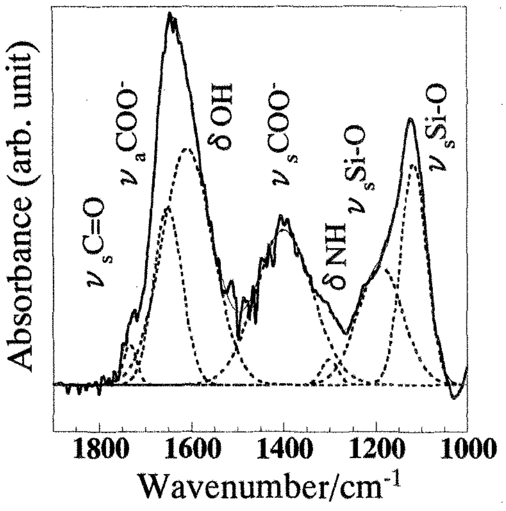

Fig. 3 FT-IR spectrum of the TiO_2 film via the precursor solution containing 2 mM EDTA and the absorbance distribution curve.

Figure 3 shows typical FT-IR spectrum taken from the TiO_2 thin film prepared from the precursor solution with 2 mM EDTA and the absorbance distribution curve obtained from the FT-IR spectrum. The carboxyl group is known to give a strong band in the range between 1735 and 1550 cm^{-1} ,which is due to the C=O stretching vibration. In this study, we can observe a band attributed to carboxyl group in EDTA at 1730 cm^{-1}. Other characteristic peaks can be seen, which arise from COO^- symmetric and asymmetric mode (1400 and 1650 cm^{-1}, respectively) and N-H bending mode (1305 cm^{-1}). The peak at ca. 1618 cm^{-1} was assigned to O-H bending mode resulting from water in the deposited film. These results are summarized in Table 1. Data for EDTA (chemical compound and adsorbed on TiO_2) are included for comparison. The spectrum obtained from this study revealed that EDTA molecules added in the precursor solution adsorb on the surface of TiO_2 in the reaction solution and are included in the deposited thin film.

Table.1 Main IR band positions of EDTA (cm^{-1}).

EDTA [20]	EDTA adsorbed on TiO_2 [21]	this study
	1731 (νC=O)	1733 (νC=O)
1620($\nu_a COO^-$)	1637($\nu_a COO^-$)	1647($\nu_a COO^-$)
1395($\nu_s COO^-$)	1404($\nu_s COO^-$)	1401($\nu_s COO^-$)
1360 (δNH^+)		1305 (δNH^+)

3.2 Gd/EDTA system

Figure 4 shows SEM images of the deposited thin films prepared from precursor solution containing 2 mM Gd/EDTA complex with various reaction times [(a) 2 hours, (b) 9 hours, (c) 15 hours, (d) 24 hours]. After the reaction for 2 hours (Fig. 4a), growth of small particles can be observed. It should be noted that the diameter of the particles is in the same order of size (approximately 50 nm). After the reaction for 9 hours (Fig. 4b), the number of visible particles in the size of 200-300 nm has increased, after reaction for 15 hours (Fig. 4c), a constant number of particles seems to grow in all three directions. After reaction for 24 hours in fig. 4d, the particles which were separated after reaction for 2 and 9 hours have now coalesced, forming uniform thin film. The surface morphology of the film reacted for 24 hours is smoother than that of the film prepared from precursor solution containing 2 mM EDTA. This result indicates that the effect of the Gd-EDTA complex on TiO_2 film deposition is less strong than that of free EDTA.

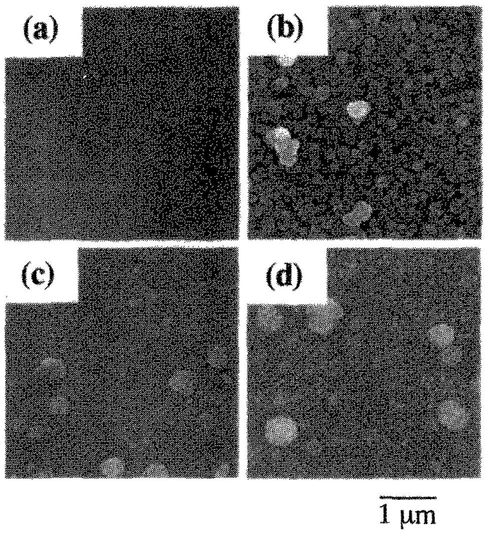

Fig. 4 SEM images of the deposited thin films via the precursor solution containing 2 mM Gd-EDTA complex with various reaction times. (a) 2 hours, (b) 9 hours (c) 15 hours, (d) 24 hours

Figure 5 shows the reaction time dependence of the deposited Gd and Ti mass on the substrate and Gd/Ti atomic ratio of the film. The Gd and Ti mass increase with increasing of reaction time. However, the drastic decrease of the Gd/Ti ratio until reacted for 12 hours is observed. A plot of this ratio vs. the reaction time indicates that most Gd-EDTA complexes accumulate rapidly on the surface of TiO_2 in the reaction solution. This result demonstrates that this rapid reaction depresses the nuclear formation on the substrate.

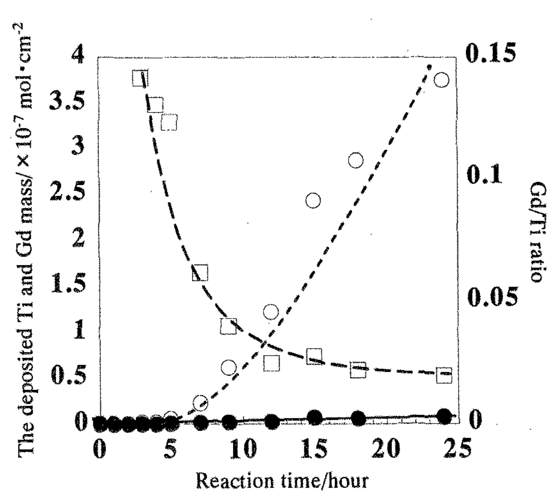

Fig. 5 Reaction time dependence of the deposited (●) Gd and (○) Ti mass on the substrate and (□) Gd/Ti atomic ratio of the film.

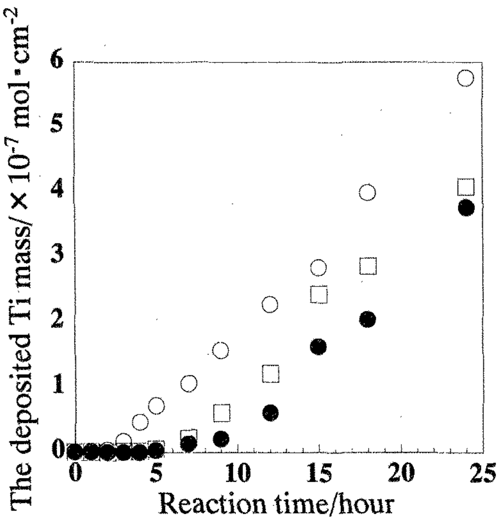

Fig. 6 Relationship between reaction time and the deposited Ti mass of the films via precursor solution containing (○) non-complexon, (□) 2 mM Gd-EDTA, (●) 2 mM EDTA.

Figure 6 shows relationship between reaction time and the amount of the deposited TiO_2 of the films prepared from precursor solution containing various kinds of complexon. The sequence of the amount of the deposited TiO_2 on the substrate is non-complexon TiO_2 >2 mM Gd-EDTA TiO_2 >2 mM EDTA TiO_2.

M. S. Vohra and A. P. Davis [22] investigated the adsorption of EDTA and Pb-EDTA onto TiO_2 and reported that adsorption of free EDTA onto TiO_2 was favorable compared to metal-complexed EDTA because all calboxylate and amine groups in the free EDTA would be available to chelate with the TiO_2 surface sites, however, the number of such coordination site in the metal- complexed EDTA was decreased.

In this study, it may be concluded that the decrease of the deposited TiO_2 mass on the substrate is due to the depression of nucleation on the substrate, which is caused by the adsorption of EDTA and Gd-EDTA complex on the deposited TiO_2 surface. The differences in the adsorbability of free EDTA and metal-complexed EDTA onto the deposited TiO_2 surface sites consequently affects on the nucleation.

4. CONCLUSION

We have investigated the addition effect of EDTA and *Ln*(EDTA)$^{n+}$ on TiO_2 film deposition by the liquid phase deposition method. The surface morphology of the films prepared from the solution with complexon was rougher than that of the films via the solution without complexon. The amount of the deposited TiO_2 on the substrate decreased with increase of the initial concentration of EDTA solution. It was considered that the decrease was caused by the depressing of the nucleation on the substrate, which was due to the adsorption of EDTA or Gd-EDTA complexon on the deposited TiO_2.

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