NAP-2013

Equilibrium Behavior for Transition Metal Ionic Species in Liquid Phase Deposition Reaction

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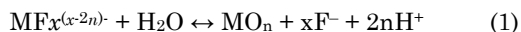*Kobe University, 1-1 Rokkodai-cho, Nada, Kobe, 657-8501 Japan*

We tried to clarify to the deposition mechanism by applying the 11B and 19F NMR analyses to the LPD reaction solutions for the preparing titanium oxide films with various reaction conditions. Moreover, the optimum conditions of the syntheses of 3d transition metal oxide thin films were investigated by controlling pH and the concentration of reacting species. In the reaction of TiO2 deposition, TiF62- do not release all F- ions, namely, the existence of hydrolysis intermediate species (TiFx(OH)y(H2O)6-x-y(4-x-y)) which could not be detected by 19F NMR because of the rapid ligand exchange in the LPD reaction solutions. In the reaction of Cr_2O_3 deposition, the optimization of the LPD reaction can be carried out by the controlling of the concentrations of reaction species and pH.

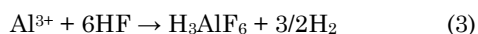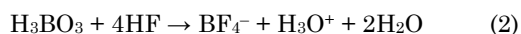## 1. INTRODUCTION

Metal oxide thin films have been widely applied as inorganic functional materials due to their electrical, optical, and magnetic properties. Recently, a novel wet process called Liquid Phase Deposition (LPD) method has attracted much attention. The LPD reaction spontaneously proceeds at ambient condition in a balance of two equilibrium reactions, which are principally described as follows: the hydrolysis equilibrium (ligand-exchange) reaction of metal fluoride complex species (eq. 1) and the F− consumption reaction with boric acid or aluminum ion as an F− scavenger (eq. 2 or 3)[1].

$$MFx^{(x-2n)\cdot} + H_2O \leftrightarrow MO_n + xF^- + 2nH^+ \qquad (1)$$

(M; e.g. Ti, Fe, Cu, Zr, Sn, W, Mo, V, Zr, Nb, Ni)

$$H_3BO_3 + 4HF \rightarrow BF_4^- + H_3O^+ + 2H_2O \qquad (2)$$

$$Al^{3+} + 6HF \rightarrow H_3AlF_6 + 3/2H_2 \qquad (3)$$

Deki et al. have adapted LPD method to the fabrication of various kinds of films, such as titanium oxide, vanadium oxide, iron oxy-hydroxide and multi component metal oxide films [2-4]. However, a small amount of fluorine is incorporated into the synthesized thin film and the essence of the deposition mechanism is still unclear. The clarification of the LPD reaction mechanism is indispensable to optimization, the high yield synthesis, and the physical properties improvement of the thin film synthesis condition. In this work, we tried to clarify to the deposition mechanism by applying the 11B and 19F NMR analyses to the LPD reaction solutions for the preparing titanium oxide films with various reaction conditions. Moreover, the optimum conditions of the syntheses of 3d transition metal oxide thin films were investigated by controlling pH and the concentration of reacting species.

2. EXPERIMENTAL

The $(NH_4)_2TiF_6$ concentrations of the parent solutions for the syntheses of TiO_2 thin films were 0.025, 0.1 and 0.2 mol L^{-1}, and the H_3BO_3 concentration was fixed at 0.2 mol L^{-1}. The degreased glass substrates were suspended vertically into the parent solution, and reacted at 30°C. The 19F NMR spectra were obtained by a Varian INOVA 400 NMR spectrometer. For the syntheses of Cr_2O_3 thin films, the $Cr(NO_3)_3$ and the HF concentrations of the parent solutions were 0.05 mol L^{-1} and 0.15 mol L^{-1}, respectively. The pH of the parent solutions were controlled by NH_3 aq., and the H_3BO_3 solution added to the final concentration of 0.25 mol L^{-1}. The degreased glass substrates were suspended vertically into the parent solution, and reacted for 24 hours at 30 °C.

3. CONTRIBUTION OF FLUORINE SCAVENGER FOR EQUILIBRIUM REACTION IN THE LPD PROCESS

Fig. 1 shows representative 19F NMR spectra of the reaction time dependence of the LPD reaction solution at the initial concentrations of 0.1 mol L^{-1} $(NH_4)_2TiF_6$ and 0.2 mol L^{-1} H_3BO_3. From the spectrum of $(NH_4)_2TiF_6$ solution, only one signal due to TiF_6^{2-} was observed, thus TiF_6^{2-} anions were quite stable in water. On the other hand, a quartet which intensity ratio was weird was observed at -149 ppm after 1 hour LPD reaction, and a doublet which was asymmetrical intensities was observed at -156 ppm after 6 hours LPD reaction, and these signals can be assigned to $BF_3(OH)^-$ and BF_4^-, respectively[5]. Free F^- anions which were produced by the hydrolysis reaction of TiF_6^{2-} were completely scavenged by H_3BO_3, hence the signal due to free F^- ions were not detected in the LPD reaction solution at each reaction time. The signals which derived from $BF(OH)_3^-$

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and $BF_2(OH)_2^-$ could not be observed because the ligand exchange of these species is much faster than NMR time scale.
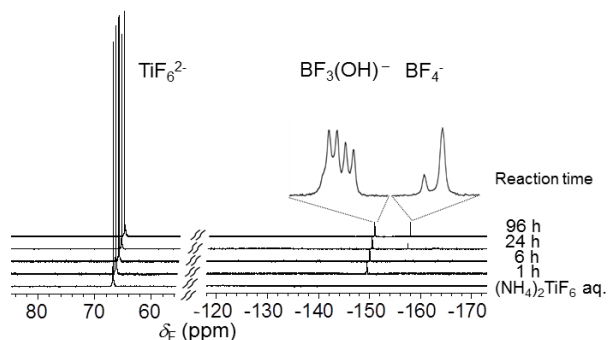

Fig. 1 – ^{19}F NMR spectra of 0.1 mol L^{-1} $(NH_4)_2TiF_6$ aq. and reaction time dependence of LPD reaction solution. $(NH_4)_2TiF_6$ aq : 0.1 mol L^{-1}. H_3BO_3 aq : 0.2 mol L^{-1}.

In order to quantitatively clarify about the deposition mechanism of titanium oxide thin films by the LPD process, the concentrations of the dissolving species in the LPD reaction solutions were determined by the comparing with the integrated intensity values of ^{19}F NMR signals of external reference. An NMR is a powerful tool for not only determination of the dissolving species but also their quantitative analysis because the integrated intensity is directly proportional to the number of resonant nuclei. Fig. 2 shows the time dependence of the concentrations of the dissolving species in the LPD reaction solutions. The relationships between the concentrations of the reactant (TiF_6^{2-}) and the products ($BF_3(OH)^-$ and BF_4^-) indicated that the most rapid reaction occurred when the initial concentration of $(NH_4)_2TiF_6$ was 0.025 mol L^{-1}, and the agglomeration of particles as the precursor of a hazy TiO_2 film was deposited. It is noteworthy that contrary to expectations the concentration of $BF_3(OH)^-$ was higher than that of BF_4^- during whole reaction time, thus, a boron molecule will scavenge not four F^- anions but three F^- anions. Since the ^{19}F NMR signals due to only TiF_6^{2-}, $BF_3(OH)^-$, and BF_4^- species were observed, if

TiF_6^{2-} ions released all F^- ions by the hydrolysis reaction as eq. (1), the following relationship will be established.

$$[TiF_6^{2-}]_{con} \times 6 = [BF_3(OH)^-]_{pro} \times 3 + [BF_4^-]_{pro} \times 4 \quad (4)$$

where $[TiF_6^{2-}]_{con}$ represents the concentration of TiF_6^{2-} consumed by LPD reaction, $[BF_3(OH)^-]_{pro}$ and $[BF_4^-]_{pro}$ represent the concentrations of $BF_3(OH)^-$ and BF_4^- produced by F^- consuming reaction, respectively. However, the concentration of F^- which was released from TiF_6^{2-} is much higher than that of F^- which was scavenged by H_3BO_3 in all concentration conditions. This result suggests that TiF_6^{2-} do not release all F^- ions, namely, the existence of hydrolysis intermediate species $(TiF_x(OH)_y(H_2O)_{6-x-y}^{(4-x-y)})$ which could not be detected by ^{19}F NMR because of the rapid ligand exchange in the LPD reaction solutions. The complicated equilibrium behaviour of these various intermediate species in the LPD reaction solutions will affect the chemical composition, the crystal structures, and the amount of yields of the metal oxide thin films.

4. SYNTHESIS MECHANISM OF CHROME (III) OXIDE THIN FILMS IN THE LPD PROCESS

Chrome (III) oxide which is the 3d transition metal oxide has many applications in a catalytic chemistry, a photolithography process and an electrode material. We also investigated the optimization of the synthesis condition of the Chrome (III) oxide thin film. Since the solubility product of $Cr(OH)_3$ is 6.3×10^{-31}, it can be expected that $Cr(OH)_3$ which is precursor of the chrome (III) oxide thin film precipitates in pH > 4.6 at $[Cr^{3+}]$ = 7.5 mmol L^{-1}.

The NH_3 concentration dependence of Cr^{3+}-HF and Cr^{3+}-HNO_3 mixture solutions as the pH of the LPD parent solutions is shown in Fig. 3. The $Cr(OH)_3$ precipitated in pH > 4.6 as expected from the solubility product in the Cr^{3+}-HNO_3 solutions, on the other hand, in the case of the Cr^{3+}-HF solution, the $Cr(OH)_3$ precipitated in pH > 6.1 against the expectation. This indicates that F^- anions which coordinates to Cr^{3+} inhibits the formation of $Cr(OH)_3$. Hence, it can be expected that the chrome (III) oxide thin film is synthesized by the LPD process

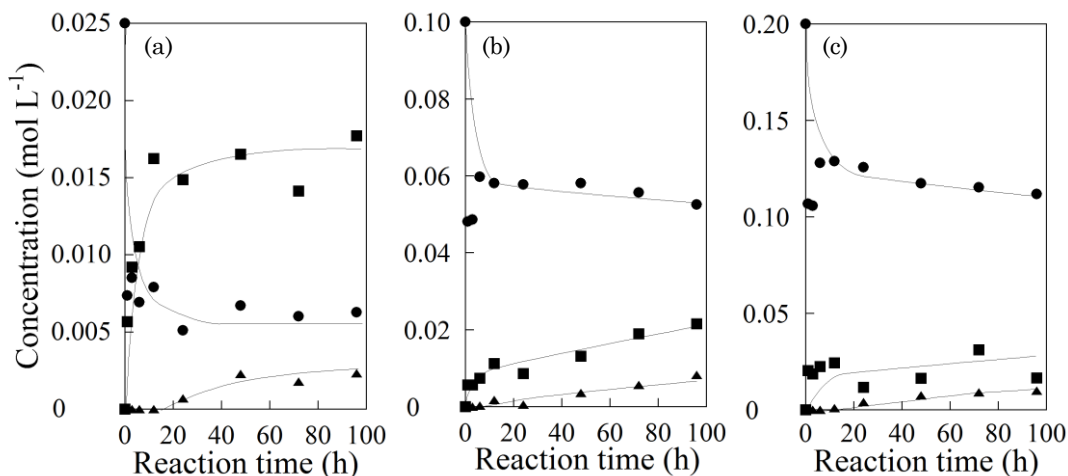**Fig. 2** – Reaction time dependence of the concentration of the dissolving species in LPD reaction solutions. $(NH_4)_2TiF_6$ aq. : (a) 0.025 mol L^{-1}, (b) 0.10 mol L^{-1}, (c) 0.20 mol L^{-1}. H_3BO_3 aq. : 0.20 mol L^{-1}. ●: TiF_6^{2-}, ■: $BF_3(OH)^-$, ▲: BF_4^-
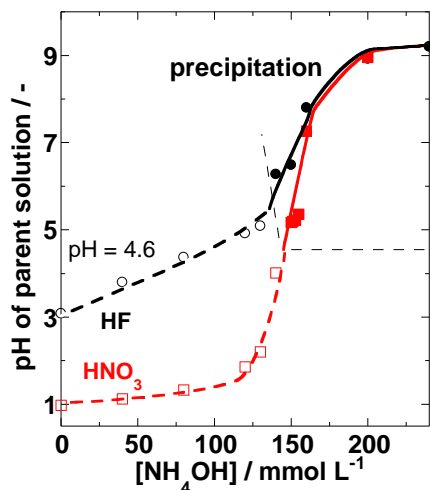
Fig. 3 – Various pH of Cr^{3+}-HF and -HNO_3 aq. with various [NH_3]. [Cr] = 7.5 mmol L^{-1}, [HF, HNO_3] = 150 mmol L^{-1}, [NH_3] = 0 − 240 mmol L^{-1}, dash line: dissolution, solid line: precipitation.

Fig. 4 – Various deposition amounts of Cr on substrates by LPD reaction with various [NH_3]. [Cr] = 7.5 mmol L^{-1}, [HF] = 150 mmol L^{-1}, [NH_3] = 0 − 130 mmol L^{-1}, reaction temp.: 30ºC and reaction time: 24 h.

when the hydrolysis of Cr^{3+} is inhibited by the coordination of F^- anions. That is to say, the addition of H_3BO_3 as a fluorine scavenger in condition that fluorine inhibits the hydrolysis of Cr^{3+} causes to slow desorption from Cr^{3+} of fluorine, and the LPD reaction proceeds and the chrome (III) oxide thin film will be deposited.

Fig. 4 shows the NH_3 concentration dependence of the deposition amounts of chromium on the glass substrates by the LPD reaction and the initial and final pHs of the LPD reaction solutions. The depositions of chrome (III) oxide thin film were observed when the hydrolysis reaction of the complex was inhibited by the coordination of F^-, i.e. pH > 4.6. Therefore, it was revealed that the optimization of the LPD reaction can be carried out by the controlling of the concentrations of reaction species and pH. The formation of the thin film of ca. 100 nm in
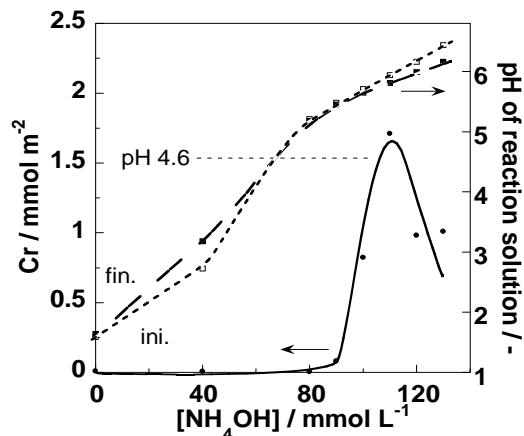
membrane thickness was confirmed by the surface observation with SEM, and it was confirmed that the composition was amorphous Cr_2O_3 with XRD and Raman spectrometry. Furthermore, the syntheses of the metal oxide thin films of Ti, V, Mn, Fe, Co, and Cu were accomplished by the appropriate control of the pH and the concentration of the reactive species in this study.

AKNOWLEDGEMENTS

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