Preparation and characterization of iron oxyhydroxide and iron oxide thin films by liquid-phase deposition

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Iron oxyhydroxide thin films have been prepared from the aqueous solution system of FeOOH–NH_4F·HF (aq.) with added boric acid by a novel liquid-phase deposition (LPD) method and is the first attempt to preparate iron oxide thin films by this method. A crystalline β-FeOOH thin film was formed directly on the substrate upon immersion into a mixed solution of FeOOH–NH_4F·HF and H_3BO_3. The orientation of the deposited film differed according to the concentration of H_3BO_3 in the solution. When the concentration of H_3BO_3 was >0.30 mol dm^{-3}, the β-FeOOH thin film was preferentially oriented in the [211] direction. The β-FeOOH thin film formed was transformed into α-Fe_2O_3 upon heat treatment in air flow. The α-Fe_2O_3 thin films obtained were oriented in the [110] direction. The F content of the as-deposited β-FeOOH film was *ca.* 15% F/Fe and was reduced to 0.19% upon heat treatment.

Generally, the preparation methods for thin films of metal oxides can be classified into physical and chemical methods. Physical methods include dry processes such as vacuum evaporation and sputtering while chemical methods include dry processes such as chemical vapor deposition and wet processes such as dipping and spin coating of sol–gel reagents. Both types of processes are widely applied to prepare many types of metal oxide thin films.

Recently, a novel wet process, liquid-phase deposition (LPD),[1,2] has been developed for the preparation of metal oxide thin films. In this process, it is possible to form thin film metal oxides or hydroxides directly on the substrate which is immersed in the treatment solution for deposition. Metal oxide or hydroxide thin films are formed by means of a ligand-exchange equilibrium reaction (hydrolysis) of a metal–fluoro complex ion and an F^- consuming reaction of boric acid or aluminium metal which act as scavengers for F^-.[1,2] In the treatment solution for deposition, a ligand-exchange equilibrium reaction (hydrolysis) of metal–fluoro complex ions, [$MF_x{}^{(x-2n)-}$], is presumed [eqn. (1)].

$$MF_x{}^{(x-2n)-}+nH_2O \rightleftharpoons MO_n+xF^-+2nH^+ \tag{1}$$

The equilibrium reaction (1) is shifted to the right-hand side by the addition of boric acid or aluminium metal, which readily react with F^- ions to form stable complex ions [eqn. (2) and (3)].

$$H_3BO_3+4HF \rightleftharpoons BF_4{}^-+H_3O^++2H_2O \tag{2}$$

$$Al+6HF \rightleftharpoons H_3AlF_6+3/2H_2 \tag{3}$$

The LPD method is a very simple process and does not require any special equipment such as a vacuum system. It can be, moreover, applied readily to the preparation of thin films on various types of substrates with large surface areas and complex morphologies, since LPD is performed in aqueous solution. So far, we have already developed and reported the preparation of titanium oxide,[3] vanadium oxide[4] and Au-dispersed titanium oxide thin films[5] by LPD.

Here, we report on the LPD method to prepare iron oxyhydroxide and oxide thin films and the characterization of the formed films. Crystalline β-FeOOH thin films were formed the aqueous system FeOOH–NH_4F·HF to which H_3BO_3 was added to act as a scavenger for F^-. On heat treatment in flowing air, the formed β-FeOOH thin film became amorphous and was transformed into α-Fe_2O_3. The formed films were characterized by XRD, IR spectroscopy, XPS and SEM observations.

Experimental

Liquid-phase deposition process

An FeOOH–NH_4F·HF aqueous solution was used as the parent solution for deposition. FeOOH was precipitated by hydrolysis of aqueous $Fe(NO_3)_2$ (Nacalai Tesque Inc.) upon addition of aqueous NH_3 (Nacalai Tesque Inc.). After filtration of the precipitate, it was washed repeatedly with distilled water and dried at ambient temperature. Then the precipitate was dissolved in 1.0 mol dm^{-3} NH_4F·HF (Nacalai Tesque Inc.) at a concentration of 0.07 mol dm^{-3}, to give the parent solution. H_3BO_3 (Nacalai Tesque Inc.), used as an F^- scavenger, was dissolved in distilled water at a concentration of 0.5 mol dm^{-3} and FeOOH–NH_4F·HF and H_3BO_3 solutions were mixed at various compositions for use as treatment solutions for deposition.

Non-alkali glass (Corning, no. 7059) was used as the substrate. After being degreased and washed ultrasonically, the substrate was immersed in the treatment solution and suspended therein vertically. Reaction was carried out at 30 °C for 20 h. The substrate was then removed from the solution, washed with distilled water and dried at ambient temperature. Heat treatments of the deposited films were carried out in an air flow for 1 h at different temperatures ranging from 100 to 600 °C.

Characterization of the deposited films

XRD studies of the deposited films were carried out on a Rigaku RINT-2100 diffractometer with a thin film attachment, using Cu-Kα radiation (40 kV, 40 mA) with measurements made at an X-ray incidence angle of 1°. Crystallite sizes of the deposited films were calculated using Scherrer's equation, $L=0.94\,\lambda/\beta\cos\theta$, where L is the mean dimension of the crystallites, β is the full-width at half-maximum in radians of the X-ray diffraction peak at the diffraction angle θ and λ is the wavelength of the Cu-Kα radiation (1.54 Å).[6] In order to calculate

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the crystallite size, the intensities were accumulated by repeating the measurement 20 times. IR spectra of the deposited films were measured with an A-302 IR spectrophotometer (Japan Spectroscopic Co. Ltd.). Fluorine and iron contents of the formed films were determined by X-ray photoelectron spectroscopy (XPS) (PHI, XPS-5600ci). Surface morphologies of the films were observed by scanning electron microscopy (SEM) (Hitachi, S-2500).

Results and Discussion

After reaction for 20 h, a transparent orange film was formed on the substrate. As shown in Fig. 1, there was a deposition region according to the concentrations of FeOOH and H_3BO_3 in the treatment solution. At low concentrations of H_3BO_3, no deposition was observed. From SEM observation of cross-sections of the films which formed at [FeOOH] = 7.0 mmol dm^{-3}, the thickness of the deposited films was *ca.* 500 nm. XRD patterns of the films formed at each point indicated in the concentration diagram (Fig. 1) are shown in Fig. 2. The diffraction peaks of each film are assigned to β-FeOOH, but the intensity distributions of diffraction peaks differ according to the concentration of H_3BO_3 in the treatment solution. At a concentration of H_3BO_3 of 0.20 mol dm^{-3} [at point (a)], the intensity distribution of diffraction peaks was in accord with reported values for a randomly oriented polycrystalline β-FeOOH powder. The intensity of diffraction from the (211) plane of β-FeOOH increased for the film formed at $[H_3BO_3] = 0.25$ mol dm^{-3} [point (b)]. When the concentration of H_3BO_3 was >0.30 mol dm^{-3} [points (c), (d) and (e)], the diffraction from the (310) plane disappeared completely, and a very intense diffraction peak from the (211) plane was observed. This indicates that the films formed at $[H_3BO_3]$ >0.30 mol dm^{-3}, are preferentially oriented in the [211] direction. Surface morphologies of the films formed at the points (b), (c) and (e) in Fig. 1 are shown in Fig. 3. The films were constructed of particles several hundreds of nm in diameter which decreased in size with increasing concentration of H_3BO_3; however, no change in surface morphology was observed. Several cracks were observed for the films formed at the points (c) and (e). It is considered that these cracks were generated by internal stress of the film due to contraction of the film upon drying.

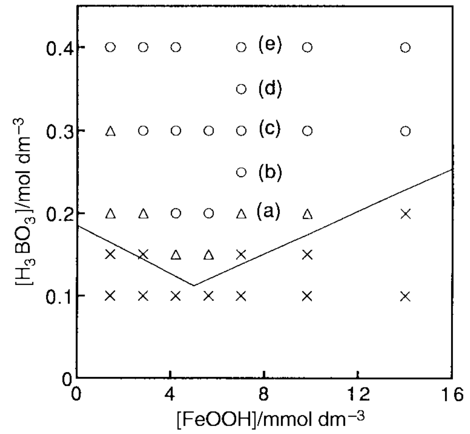

Fig. 1 Relationship between the aspect of the deposited film and the concentrations of FeOOH and H_3BO_3. ○, Transparent β-FeOOH; △, hazy β-FeOOH; ×, no deposition. Reaction time: 20 h.

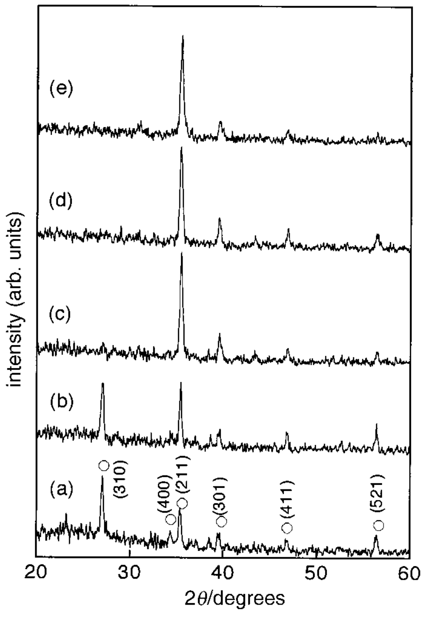

Fig. 2 X-Ray diffraction patterns of the films formed at the points indicated in Fig. 1. ○, β-FeOOH. [FeOOH] = 7.0 mmol dm^{-3}; $[H_3BO_3]$ = (a) 0.2, (b) 0.25, (c) 0.30, (d) 0.35 and (e) 0.40 mol dm^{-3}. Reaction time: 20 h.

We can propose a plausible mechanism for the formation of β-FeOOH thin films by LPD. Iron(III) ions, Fe^{3+}, in the treatment solution are coordinated by fluorine ions to give species $[FeF_6]^{3-}$ and/or $[FeF_{6-n}(OH)_n]^{3-}$. Following F^- release [eqn. (4) and (5)], reaction proceeds leading to film formation.

$$[FeF_6]^{3-} + nH_2O \rightleftharpoons [FeF_{6-n}(OH)_n]^{3-} + nHF \qquad (4)$$

$$[FeF_{6-n}(OH)_n]^{3-} + nH_2O \rightleftharpoons [Fe(OH)_6]^{3-} + nHF \qquad (5)$$

The ligand-exchange equilibrium reactions (hydrolysis) (4) and (5) are shifted to the right-hand side upon the addition of boric acid which readily reacts with F^- [eqn. (2)].

Addition of boric acid to the treatment solution leads to consumption of F^- ions and accelerates the ligand-exchange of $[FeF_6]^{3-}$ and $[FeF_{6-n}(OH)_n]^{3-}$. The species $[Fe(OH)_6]^{3-}$ is subsequently dehydrated on the surface of the substrate leading to the formation of an iron oxyhydroxide thin film.

It is well known that the presence of Cl^- or F^- ions during hydrolysis of Fe^{3+} results in formation of β-FeOOH rather than α-FeOOH[7–9] and large numbers of investigations related to the formation of β-FeOOH by hydrolysis of aqueous $FeCl_3$ have been made. According to these investigations, the crystal structure of β-FeOOH has tunnels parallel to the *c*-axis, within which water molecules and Cl^- ions are accommodated.[9–12] In our films F^- ions are accommodated in the tunnels of β-FeOOH. XPS indicates an F content of 14.8 and 14.7% F/Fe for films formed at the points (b) and (c) in Fig. 1, respectively, indicating that the F content in the deposited film was independent of the concentration of H_3BO_3 in the treatment solution. Some F^- ions also exist at the surfaces of the crystals of β-FeOOH.

Fig. 4 shows XRD patterns of films [at point (c) of Fig. 1] which have been heat-treated at various temperatures for 1 h *i.e.* (211) oriented β-FeOOH films. Transformation into α-Fe_2O_3 upon heat treatment occurs with a change of the colour from yellowish to reddish. Upon the heat treatment at 100 °C, the intensities of the diffraction peaks were reduced, but no change in crystal phase was observed. Only one broad and low-intensity XRD peak was observed for films heat-treated at 200–500 °C. Upon heat treatment at 600 °C, the film was completely transformed into α-Fe_2O_3. Ishikawa and Inouye[10,11] reported that β-FeOOH changes into an amorphous mixture of β-FeOOH and α-Fe_2O_3 in the temperature range 200–300 °C, and is transformed into crystalline α-Fe_2O_3 above 400 °C. The crystallite size calculated using Scherrer's equation[6] for the diffraction peak at *ca.* 35° [diffraction from the (211) plane for β-FeOOH and the (110) plane for α-Fe_2O_3] is shown

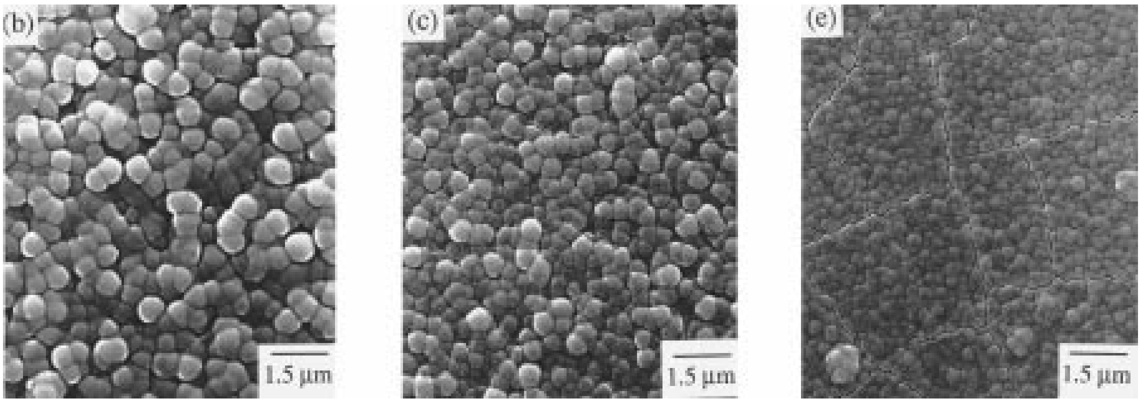

Fig. 3 SEM photographs of the films formed at the points indicated in Fig. 1. [FeOOH] = 7.0 mmol dm^{-3}; [H_3BO_3] = (b) 0.25, (c) 0.30 and (e) 0.40 mol dm^{-3}. Reaction time: 20 h.

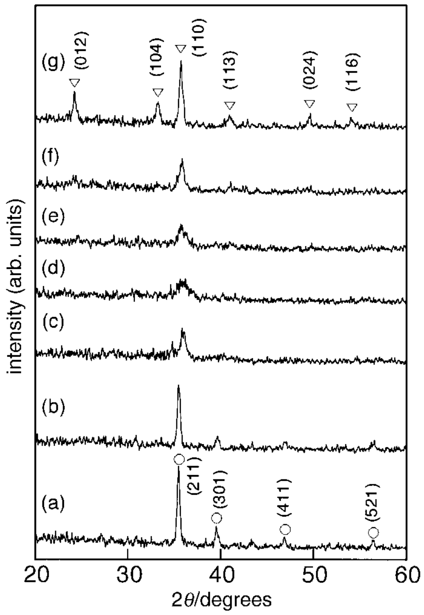

Fig. 4 X-Ray diffraction patterns of the deposited films heat-treated at various temperatures for 1 h. (a) As-deposited film; (b)–(g) films heat-treated at 100, 200, 300, 400, 500 and 600 °C, respectively. ○, β-FeOOH; ▽, α-Fe_2O_3. [FeOOH] = 7.0 mmol dm^{-3}; [H_3BO_3] = 0.30 mol dm^{-3}. Reaction time: 20 h.

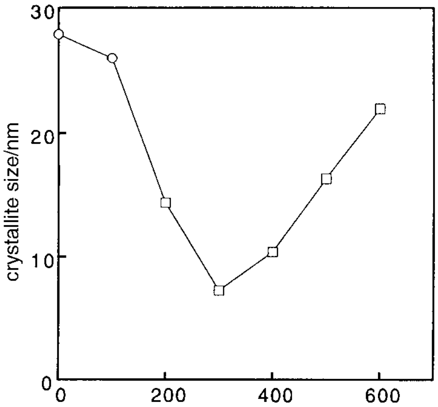

Fig. 5 Relationship between the crystallite size and heat-treatment temperature. ○, Calculated for the diffraction from the (211) plane of β-FeOOH and □, from the (111) plane of α-Fe_2O_3. [FeOOH] = 7.0 mmol dm^{-3}; [H_3BO_3] = 0.30 mol dm^{-3}. Reaction time: 20 h.

in Fig. 5. The crystallite size decreased with increasing heat-treatment temperature up to 300 °C, and thereafter increased. The decrease of the crystallite size is due to destruction of the structure of β-FeOOH, while the subsequent increase of crystallite size is due to the crystal growth of α-Fe_2O_3. The intensity distribution of the diffraction peaks of the film heat-treated at 600 °C is different from that of randomly oriented powder of α-Fe_2O_3. The diffraction from the (110) plane is particularly intense, indicating that the film is partially oriented in the [110] direction.

Fig. 6 shows SEM photographs of films heat-treated at 200, 400 and 600 °C; no morphological change is observed upon heat treatment.

Fig. 7 shows the F/Fe atomic ratio of the films formed at the point (c) in Fig. 1 as a function of heat-treatment temperature. The F content in the deposited film is constant below 100 °C, decreased rapidly with increasing temperature in the range 100–300 °C and then decreased more gradually with temperature up to 600 °C. It is presumed that β-FeOOH contains two kinds of F^- ions, one type which can be readily removed and the other which is strongly bound to Fe. The former presumably exist on the surface of the crystals and the latter are accommodated in the tunnels of β-FeOOH.[13] The F content of the film heat-treated at 600 °C was 0.19% F/Fe.

IR spectra of the deposited films heat-treated at various temperatures are shown in Fig. 8. The spectra were measured by the conventional KBr method for the films scratched from the substrates. IR spectrum of the as-deposited film has absorption bands at 700 and 450 cm^{-1}, which are assigned to the Fe–OH deformation mode[11,14] and the lattice vibration of β-FeOOH,[13] respectively. Ishikawa and Inouye[11] reported that β-FeOOH shows absorption bands at 840, 690 and 640 cm^{-1} which are assigned the deformation mode of Fe–OH groups. The absorption bands at 840 and 640 cm^{-1} diminished with removal of Cl^- ions within the tunnels of β-FeOOH. Ishikawa and co-workers[15,16] explained the diminution of the absorption bands at 840 and 640 cm^{-1} as follows. In β-FeOOH, Fe–OH groups exist in the walls of the tunnels of the crystal. Since Cl^- ions and water molecules also exist in the tunnels, there are therefore two types of Fe–OH groups, one of which interacts with Cl^- and the other which interacts with water molecules. The absorption bands at 840 and 640 cm^{-1} which diminished with removal of the Cl^- ion are assigned to the deformation band of Fe–OH groups interacting with Cl^- ions. In the present spectra (Fig. 8), no bands at 840 and 640 cm^{-1} were observed. While the details are unclear at present, it is considered that differences in interactions between water molecules with Cl^- and F^- lead to the difference in IR absorption bands. For films heat-treated at 200 and 400 °C, the absorption bands became broad, and the absorption band at 700 cm^{-1} disappeared. The IR spectrum of the film heat-treated at 600 °C

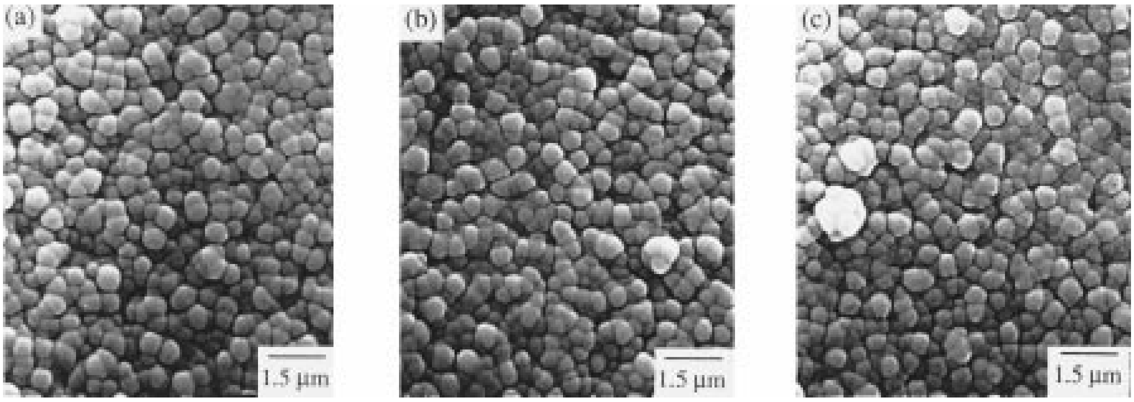

Fig. 6 SEM photographs of the films heat-treated at 200 (a), 400 (b) and 600 °C (c). [FeOOH] = 7.0 mmol dm^{-3}; [H_3BO_3] = 0.25 mol dm^{-3}. Reaction time: 20 h.

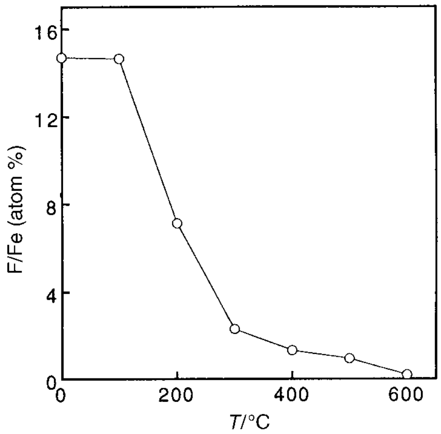

Fig. 7 F contents in the deposited films heat-treated at various temperatures. [FeOOH] = 7.0 mmol dm^{-3}; [H_3BO_3] = 0.30 mol dm^{-3}. Reaction time: 20 h.

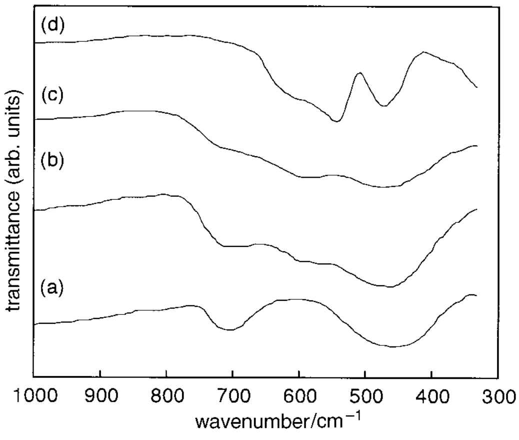

Fig. 8 IR spectra of the deposited films heat-treated at various temperatures for 1 h. (a) As-deposited film; (b)–(d) films heat-treated at 200, 400 and 600 °C, respectively. [FeOOH] = 7.0 mmol dm^{-3}; [H_3BO_3] = 0.30 mol dm^{-3}. Reaction time: 20 h.

showed absorption bands at 540 and 470 cm^{-1}, which are characteristic of α-Fe_2O_3.[13,17]

Conclusion

The LPD method was applied to the preparation of iron oxyhydroxide and oxide thin films. The crystalline β-FeOOH thin film was formed by the LPD method from a mixed solution of FeOOH–$NH_4F{\cdot}HF$ and H_3BO_3 at ambient temperature. The F content of the formed film was *ca.* 15% F/Fe. XRD measurements revealed that the film deposited at higher concentrations of H_3BO_3 was oriented to the [211] direction. In contrast the formed film was randomly oriented when the concentration of H_3BO_3 was low.

On heat treatment in an air flow, the deposited film (crystalline β-FeOOH) became amorphous and was transformed into α-Fe_2O_3 completely at 600 °C. The F/Fe atomic ratio of the deposited film decreased with increasing heat-treatment temperature, and was 0.19% for the film heat-treated at 600 °C.

We propose the following reaction mechanism for the deposition of iron hydroxide thin films by the LPD method. In the treatment solution, Fe^{3+} exists as $[FeF_6]^{3-}$ or partially hydrolyzed species $[FeF_{6-n}(OH)_n]^{3-}$. The ligand-exchange reaction (hydrolysis) of such species was accelerated by the addition of H_3BO_3 as scavenger for F^-. Then dehydration of $[Fe(OH)_6]^{3-}$ occurs at the surface of the substrate and consequently, iron oxyhydroxide thin films are formed on the immersed substrate.

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