

Fabrication of Copper Ferrite Thin Films from Aqueous Solution by the Liquid-phase Deposition Method

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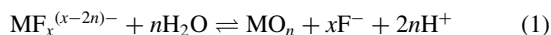
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Liquid-phase deposition, LPD, method was used for the fabrication of copper ferrite (CuFe_2O_4) thin film from aqueous solution system of $\text{FeOOH}\cdot\text{NH}_4\cdot\text{HF}$ (aq.) and Cu source ($\text{Cu}(\text{NO}_3)_2$ or CuCl_2) with H_3BO_3 . SEM observation revealed that highly homogeneous thin film was formed on a substrate. In X-ray diffraction measurements, major peaks assigned to CuFe_2O_4 was observed in heat-treated films. Quantitative analysis of elements in the deposited films indicated the deposition of CuFe_2O_4 . The kinds of Cu-source did not affect on the deposition. Initial content of Cu^{2+} could alter the Fe/Cu atomic ratio in deposited film.

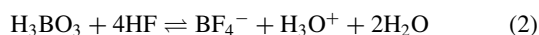
Metal ferrites, MFe_2O_4 , are one of the important materials, because of their potential applications for electronic, catalytic, and magnetic materials. Especially, copper ferrite; CuFe_2O_4 has a spinel structure, and expected to be applied for magnetic materials. Although ferrites are traditionally prepared in bulk form by a dry process, the miniaturization of magnetic and electronic devices has desired to develop advanced materials with novel morphologies, such as nanoparticles or nano-structured thin films.

Generally, fabrications of copper ferrite films are accomplished by chemical vapor deposition,¹ electrodeposition,² spin coating and sol-gel method.³ These processes are widely applied to preparing various kinds of metal oxides. However, there are some problems, that make it difficult to control precisely the composition of metal oxides, and require special apparatuses for the fabrication. Also they are not suitable for the preparation of thin films on a substrate with large surface areas and complex surface morphology, because these methods usually need a high vacuum or a low-pressure atmosphere.

In recent years, we have developed and reported a chemical method to fabricate thin films on various substrates, called liquid-phase deposition (LPD) method.⁴ In the method, metal oxide or metal hydroxide thin films are formed on the substrate through the ligand exchanging equilibrium reaction of metal-fluoro complex and the F^- consumption reaction by adding of F^- scavenger.



The eq 1 is shifted toward the right side by the addition of boric acid, which readily reacts with F^- and forms a more stable complex as following eq 2.



The method has enabled us to fabricate thin films of metal oxides at an ambient temperature and atmosphere. Moreover, it would be readily applied to various kinds of substrate with large surface areas and complex surface morphologies.⁵ Also, multicomponent oxide thin films can be easily obtained by

mixing solution of objective metal ions. Because the LPD method is performed in the aqueous system, which is typically homogeneous. In this paper, we report the fabrication of copper ferrite (CuFe_2O_4) thin films by the LPD method. The effect of counter ions of Cu source in reaction mixture was also investigated.

α - FeOOH was dissolved into a solution of 1.0 mol dm^{-3} $\text{NH}_4\text{F}\cdot\text{HF}$ at a concentration of 0.07 mol dm^{-3} , and apply to a precursor solution. As a solution of copper, $\text{Cu}(\text{NO}_3)_2$ or CuCl_2 was dissolved into distilled water at a concentration of 0.05 mol dm^{-3} . H_3BO_3 aqueous solution was used at a concentration of 0.5 mol dm^{-3} .

The concentration of LPD aqueous mixture was constant as follows; $[\text{Fe}^{3+}]$, 5 mmol dm^{-3} , $[\text{Cu}^{2+}]$, 2 mmol dm^{-3} , $[\text{H}_3\text{BO}_3]$, 0.2 mol dm^{-3} , respectively. Soda lime glass was used as the substrate. After degreased and washed ultrasonically, the substrate was immersed into the mixture and suspended vertically. Fabrications of thin-films were carried out at 30°C for various reaction times. After removed from the mixture, the substrate was washed with water and dried. Heat treatments of the obtained films were carried out at 600°C under air flow for an hour.

The amount of Fe and Cu contained in the deposited film was obtained with ICP-AES ULTIMA-2000 (HORIBA). The morphology of deposited films was observed with scanning electron microscopy (FE-SEM; JEOL, JEM-6335F). X-ray diffraction measurements for the deposited films were carried out with a Rigaku RINT-TTR diffractometer, using $\text{Cu K}\alpha$ radiation.

Figure 1a shows top-down SEM image of deposited thin-film. Highly homogeneous films with spindle-like particle, Figure 1a are observed on the surface of substrate in all cases. The shapes of particle on the obtained films are different from that of β - FeOOH thin film. Further, it is observed that a crystal lattice on high-resolution TEM images (Figure 1b). The lattice spacing was 0.25 nm , which agrees with that of $\text{CuFe}_2\text{O}_4(311)$. From cross sectional SEM and TEM observation, the film thickness was approximately 200 nm after 9 h of deposition.

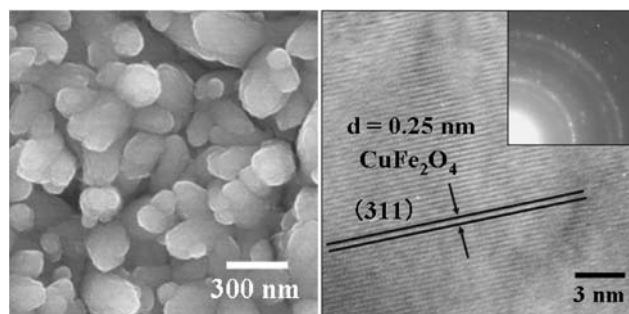


Figure 1. Photographs of heat-treated CuFe_2O_4 thin film. (a): SEM, (b): TEM and corresponding selected area electron diffraction (SAED) pattern (inset).

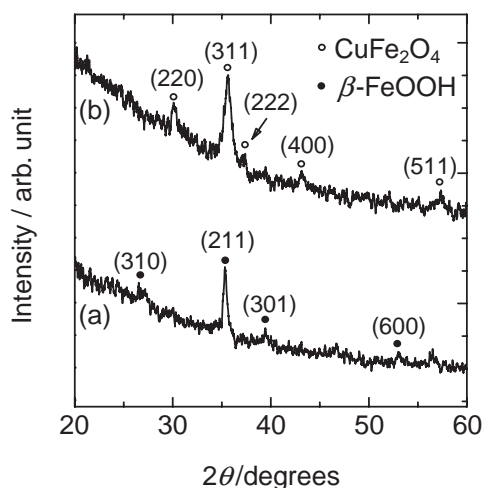


Figure 2. XRD patterns of deposited film. (a) As-deposited, (b) calcinated at 600 °C.

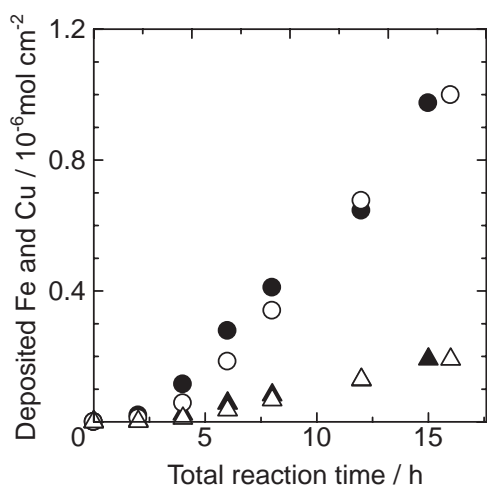


Figure 3. Relationship between the amount of deposited Fe and Cu. Fe and Cu in the films are displayed with circle and triangle symbol, respectively. Solid (CuCl_2) and hollow ($\text{Cu}(\text{NO}_3)_2$) indicates kind of Cu source.

Figure 2 shows the XRD patterns for as-deposited and calcinated films. The XRD patterns for as-deposited film give β -FeOOH peaks. For calcinated film, the patterns of CuFe_2O_4 are observed and all peaks are assigned to those of CuFe_2O_4 (JCPDS 25-283), which clearly indicates the formation of a spinel-type structure. Moreover, no other peaks can be associated to other phases such as CuO or Fe_2O_3 . These results lead us that CuFe_2O_4 thin film would be prepared.

The variation of Fe and Cu content in deposited film with reaction time is shown in Figure 3. First stage of reaction, induction period of film deposition is confirmed. In this period, film deposition rate on the substrate is slightly low. Thereafter, the

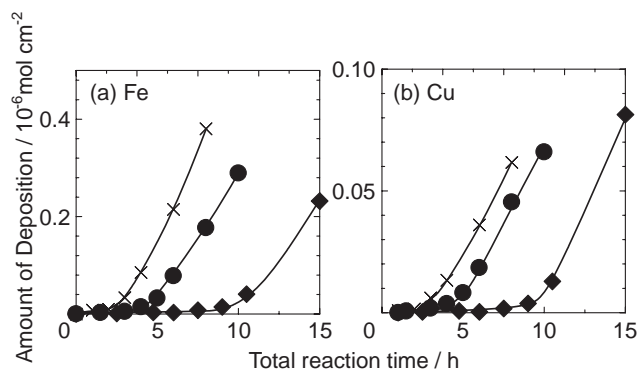


Figure 4. Plots of the amount of (a) Fe and (b) Cu in the films vs reaction time. Films were deposited at initial concentration of Cu^{2+} : \times : 1, \bullet : 3, \blacklozenge : 7 mmol dm^{-3} in reaction mixture.

amount of deposition increases linearly with reaction time.

In addition, the effect of starting material for Cu source was also investigated. As a Cu source, $\text{Cu}(\text{NO}_3)_2$ or CuCl_2 was used. A closely similar result is obtained in terms of induction period, deposition rate, and Fe/Cu atomic ratio in the films (Figure 3). Also, SEM images show spindle-like particles in all cases. Furthermore, XRD patterns for both films also indicate that CuFe_2O_4 is formed after heat-treatment. Hence, the chemical compounds for Cu-source would not affect the depositing process.

Figure 4 shows the amount of deposited Fe and Cu plotted as a function of total reaction time with various Cu^{2+} initial concentrations. Increase with Cu^{2+} concentration in reaction mixture, induction period of Fe and Cu deposition are extended in a similar manner. Interestingly, high concentration of Cu^{2+} in reaction mixture serves to slow down the rate of Fe content, while that of Cu has no significant change.

We prepared CuFe_2O_4 thin film by the LPD method from aqueous solution. The kind of Cu-source did not affect the deposition process. Initial content of Cu^{2+} could alter the Fe/Cu atomic ratio in deposited film.

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