LOW TEMPERATURE FERRITE FILM PREPARATION
BY FERRITE PLATING TECHNIQUE

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Abstract--- Ferrite plating facilitates formation of polycrystalline spinel ferrite films ($\text{Fe}_{3-x}\text{M}_x\text{O}_4$, $\text{M}=\text{Fe}, \text{Co}, \text{Ni}, \text{Zn}$, etc.) at low temperature in an aqueous solution. Though prepared at low temperature ($<90^\circ\text{C}$), the magnetic properties of the films are as good as those in bulk samples, the ferrite plating opening the door to new ferrite film devices using a non-heat-resistant substrate. In this paper we describe the principle and methods of ferrite plating, and report structural and magnetic properties of the films as well as the deposition rate of the films in connection with the conditions under which the ferrite plating is performed.

1. INTRODUCTION

Ferrite plating invented by the authors facilitates the formation of crystalline spinel films in an aqueous solution below 90°C [1]-[4]. While conventional electro or electroless plating make metal films, our ferrite plating makes oxide films with spinel structure. The plated films of the spinel, $\text{Fe}_{3-x}\text{M}_x\text{O}_4$, can contain various transition metal ions (e.g., $\text{M}=\text{Ni}, \text{Co}, \text{Zn}, \text{Mn}$, and Cr ; or mixture of there metal ions). Though prepared at low temperature, the ferrite plating films are good in crystallinity, having magnetic properties as good as those of bulk samples. Thus the ferrite plating opened the door to make the new ferrite film devices: magnetic capsule toner and carrier for zerography and magnetography in which polymer microspheres are coated with ferrite [11], and non-reciprocal ferrite devices such as circulator fabricated on GaAs MMIC which deteriorates when heated above 300°C [5], [8].

The ferrite plating films show good affinity with such organic materials as dextran and sucrose [7]. Fixing a enzyme (urease or glucose oxidase) on the Fe_3O_4 films intermediated by dextran layer, we have successfully made biosensors which detect biomaterial (i.e., urea or glucose) in a biosolution [11].

This paper describes the principle and experimental methods of ferrite plating, and presents the structure and magnetic

properties of the films of $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ ($x \leq 0.43$), $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$ ($x \leq 0.93$), and $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$ ($x \leq 0.8$) prepared by the ferrite plating.

2. PRINCIPLE OF FERRITE PLATING

A substrate with OH-groups on the surface is soaked in a reaction solution containing Fe^{2+} and other metal ions such Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} [1]. Then the metal ions are adsorbed on the surface intermediated by the OH-groups. By introducing an oxidizing reagent, such as air, NO_3^- , NO_2^- , ClO_4^- or anodic current (which is applicable only for Fe_3O_4 film with metallic conductivity), into the solution, some of the adsorbed Fe^{2+} ions are oxidized to Fe^{3+} . This causes ferrite formation reaction. Since the ferrite layer thus formed has also OH-groups on the surface, the ferrite formation reaction is repeated to grow the ferrite film. The ferrite formation occurs in the aqueous solution at $\text{pH}=6-11$ and $T>60^\circ\text{C}$.

3. EXPERIMENTAL

3.1 Preparation of Aqueous Solution

The reaction solution is prepared from FeCl_2 , CoCl_2 , NiCl_2 , and ZnCl_2 by dissolving them together with $\text{CH}_3\text{COONH}_4$ (which works as a pH buffer and also a complexing agent) in distilled water [2]-[4], [6]. The pH value of the solution is adjusted to a desired value (5-8) by adding NaOH or NH_3 solution.

The oxidizing solution used in this study is prepared by dissolving NaNO_2 and $\text{CH}_3\text{COONH}_4$ in distilled water.

3.2 Plating Methods

We have developed several methods for performing ferrite plating. In the early stage of our study, we performed the ferrite plating by "air-bubbling" and "rotating disc" methods [2], in which air is used as an oxidizing reagent. In these methods film deposition rate is very low (2 nm/min) and the film quality is deteriorated, because the ferrite powders formed in the reaction solution stick to the film surface. In order to correct the defects, we invented "thin liquid-film" method, in which the reaction and oxidizing solution are flowed through the narrow space between the substrate surface and the cell wall (Fig. 1 (a)) [3]. The ferrite particles formed in the solution are rinsed off, prevented from sticking to the film surface. This improves the film quality.

Fig. 1 (a) "Thin liquid-film" method [3] and (b) "spin-spray" [4], [6] method for ferrite plating.

Furthermore, by using NaNO_2 solution instead of air as the oxidizing solution, we have improved the film deposition rate by a factor 8-10. Using the NaNO_2 solution also facilitates a precise control of the oxidizing rate in the ferrite formation reaction.

In order to further improve the film quality and to extend the size of the substrate up to 8" diameter, we invented "spin-spray" method [4], [6]. The reaction and oxidizing solution are simultaneously sprayed onto the spinning substrate as shown in Fig. 1 (b). This facilitated formation of ferrite films with a mirror luster on a 8" glass disc.

To increase the solubility limit of such particular metal ions as Ni^{2+} and Mn^{2+} in the plated film, we have performed the plating at elevated temperatures $T=100\text{--}200^\circ\text{C}$ [12]. We call this method as "hydrothermal" method, because the pressure inside the reaction cell (which is essentially similar as is used in the "thin liquid-film" method) is kept sufficiently high (15-20 kgf/cm²) to prevent the mixed aqueous solution from boiling.

4. DEPOSITION RATE AND PROPERTY OF FILM

4.1 Chemical Composition of Film

As Fig. 2 shows, the chemical composition of the plated films deviates from that of the reaction solution [6]. The Zn composition, x , in $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$ film (curve (a)) is extremely larger than that in the reaction solution, while Ni composition, x , in $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$ film (curve (b)) is much smaller than that in the solution, though

Fig. 2 Composition x in films of (a) $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$ (plating conditions: pH=6.9, $T=80^\circ\text{C}$), (b) $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$ (pH=6.9, $T=80^\circ\text{C}$) and (c) $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$ (pH=7.0, $T=200^\circ\text{C}$) plotted as a function of x in reaction solution.

all the films are plated on the same conditions (i.e., pH=6.9 and T=80 °C). This is because at pH=6.9 the rate of the adsorption of the Zn^{2+} (Ni^{2+}) ions is much higher (smaller) than that of the Fe^{2+} ions.

The Ni concentration is increased by elevating the plating temperature from 80 °C (curve (b)) to 200 °C (curve (c)) [12]. This is because the number of the Fe^{2+} ions, which compete with the Ni^{2+} ions in entering into the spinel lattice, decreases at the high temperature where the rate of the $Fe^{2+} \rightarrow Fe^{3+}$ oxidation increases.

Fig. 3 (a) X-ray line intensity ratios I_{100}/I_{311} and I_{111}/I_{311} for Fe_3O_4 and $Fe_{3-x}Co_xO_4$ ($x=0.43 \pm 0.03$) films, respectively, plotted vs. $NaNO_2$ concentration in oxidizing solution [10]. (b) X-ray line intensity ratio I_{111}/I_{311} for $Fe_{3-x}M_xO_4$ ($M=Ni, Co, Zn$) films, plotted vs. x in film [10], [6].

4.2 Deposition Rate and Structure of Film

All the plated films are polycrystalline with spinel structure.

The deposition rate of film increases as the $NaNO_2$ concentration in the oxidizing solution increases. For good quality film of single phase spinel, we get maximum rate of 30 nm/min and 20 nm/min by the "thin liquid-film" [3] and "spin-spray" method [4], respectively.

As Fig. 3 (a) shows, the film of Fe_3O_4 and $Fe_{3-x}Co_xO_4$ exhibit preferential crystallographic orientation along (100) and (111) planes, respectively, parallel to the surface. This texture is most prominent when the $NaNO_2$ concentration is 1.0 and 1.5 g/l, respectively [10]. Not only Co^{2+} but also Ni^{2+} and Zn^{2+} causes the (111) texture as their concentrations in the film increase (Fig. 3 (b)) [6].

4.3 Magnetic Properties

As measured by a vibrating sample magnetometer, the magnetization in all the plated films lies in the film plane due to demagnetizing field. The values of the saturation magnetization in the $Fe_{3-x}M_xO_4$ ($M=Fe, Co, Ni$, and Zn) films coincide with those expected for the bulk samples [3], [6]. The ferrite plating films have good crystallinity, even though they are prepared at low temperature (<90 °C).

As shown in Fig. 4, the coercive force parallel to the film plane in $NiZn$ -ferrite [5], magnetite [4], and Co -ferrite [10] films are 31 Oe, 160 Oe, and 615 Oe, respectively. The strong coercive forces in the magnetite and Co -ferrite films are ascribed to the Fe^{2+} and Co^{2+} ions with anisotropic electron clouds. Thus we can prepare soft and hard magnetic films by ferrite plating.

When dextran ($(C_6H_{10}O_5)_n$, $n=1200-1800$) solution is added to the reaction solution in the Fe_3O_4 plating by "spin-spray" method, coercive force as well as saturation magnetization reduces [9]. Dextran reduces and increases the amounts of Fe^{2+} and Fe^{3+} , respectively, changing the chemical composition of the film from Fe_3O_4 to γ - Fe_2O_3 .

5. CONCLUDING REMARKS

By ferrite plating we have made magnetic films of compositions $Fe_{3-x}M_xO_4$,

Fig. 4 Magnetization curves for (a) $\text{Fe}_{2.47}\text{Ni}_{0.28}\text{Zn}_{0.25}\text{O}_4$ [5] and (b) Fe_3O_4 [4] films formed by "spin-spray" method, and (c) $\text{Fe}_{2.57}\text{Co}_{0.43}\text{O}_4$ [10] films formed by "thin liquid-film" method, measured parallel (//) and perpendicular (⊥) to the film plane.

where $M = \text{Fe, Co, Ni, Mn, and Zn}$. The films are polycrystalline with spinel structure. They tend to exhibit a (100) or (111) texture depending on their chemical composition and the concentration of NaNO_2 in the oxidizing solution. Though prepared at low temperature ($<90^\circ\text{C}$), the films have magnetic properties as good as those in bulk samples, showing that the films are crystallized well.

There are several methods to perform the ferrite plating, among which the "spin-spray" and the "thin liquid-film" methods are most advantageous to get good quality films. The latter is extended to the "hydrothermal" method, in which the films are plated at $T=100\text{--}200^\circ\text{C}$ and $P=10\text{--}15\text{kgf/cm}^2$. This method increase the solubility limit of such particular ion as Ni^{2+} in the spinel much.

The deposition rate of the film in the ferrite plating is $20\text{--}30\text{ nm/min}$. We found recently that we can enhance the deposition rate more than several times when the substrate is heated optically instead of using a resistance heater. We call this "light-enhanced" method, which we expect to bring about a new development in the ferrite plating technique.

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