

Electro-Ferrite Plating of Fe₃O₄ Films from Aqueous Solutions of FeCl₂ Mixed with Various pH-Adjusting Solutions

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Applying anodic voltage of $V_a=0.2\sim0.4V$, single phase magnetite films are grown at 80°C on Cu and NESA-glass substrates from aqueous solutions (pH=5~7) of FeCl₂ + CH₃COONH₄, NH₃, NaOH or KOH. The electro-plated magnetite films have saturation magnetization of magnetite equal to that of bulk sample. The highest deposition rate of 27.9nm/min is obtained at $V_a=0.4V$ and pH=6.9 from FeCl₂(30mmol/l) +NH₃(26.6mmol/l). Films having the smoothest film surface are obtained under the same conditions except the concentration of NH₃ is reduced to 23.6mmol/l.

1. INTRODUCTION

By ferrite plating, we can prepare polycrystalline ferrite films of spinel type, (Fe, M)₃O₄ (M= Fe, Ni, Co, Mn, Zn, etc.), directly from an aqueous solution at temperatures below 100°C¹⁻⁴. In ferrite plating Fe²⁺ ions are oxidized to Fe³⁺ either chemically by oxidizing reagents such as NaNO₂ and O₂, or electrochemically by anodic current. The former (electroless ferrite plating) is applicable to various spinels including Fe₃O₄, but the latter (electro-ferrite plating) only to magnetite (Fe₃O₄) which has a high electric conductivity. Extensive studies have been done on electroless ferrite plating of Fe₃O₄, but not on electro-ferrite plating of Fe₃O₄. In this study, we investigated conditions on which magnetite films are synthesized by electro-ferrite plating and examined how surface smoothness and deposition rate depend on the conditions.

2. EXPERIMENTAL

Electro-ferrite plating was performed at 80°C in a vessel (30ml in volume) shown in Fig.1. A pair of Cu plates (10×30×0.1mm³) or a pair NESA glass plates (10×30×1mm³, Takahashi Giken Glass Co. Ltd.) having transparent electro-conducting ITO coating (~30Ωcm) was used as electrodes

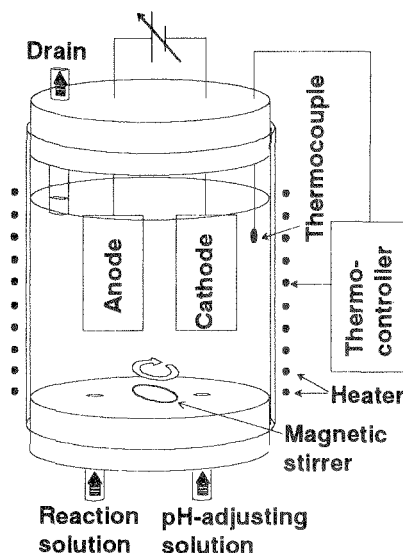


Fig.1 Apparatus used for electroplating of magnetite.

(substrates worked as anode electrodes). After treated with oxygen plasma on their surfaces, the electrodes were immersed in a mixed solution of FeCl₂ and pH-adjusting solution of various kinds, as shown in Table I. Both the reaction solution and the pH-adjusting solution were supplied into

Table I Aqueous solutions used for electro-plating of Fe₃O₄.

	Reaction solution		pH-adjusting solution		
	FeCl ₂	CH ₃ COONH ₄	NH ₃	NaOH	KOH
Concentration (mmol/l)	30	63~1890	11.8~443	12.5~37.5	5~25
pH in mixed solution	—————	5.0~6.65	4.0~10.0	3.7~7.3	3.3~7.2

the vessel at the same flow rate of 5cc/min. Applying various values of voltage, $V_a=0.2-0.8V$, to the electrodes for 50–180min, we obtained film coatings on the anodic electrodes. The films were subjected to X-ray diffraction (XRD) analyses using $CuK\alpha$ radiation and magnetic measurements using a vibrating sample magnetometer. Surface smoothness and film thickness were examined by a scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

First we fixed the concentration of $FeCl_2$ at $C(FeCl_2)=30mmol/l$ and investigated the conditions under which magnetite films are obtained. Films of single phase magnetite (as examined by XRD) are obtained on both Cu and NESA-glass substrates at $V_a=0.2-0.4V$ and $pH=3.5-7.5$ for NH_3 , $NaOH$ or KOH ; and at $pH=5.0-6.2$ for CH_3COONH_4 . Figure 2 shows relative magnitudes of X-ray diffraction, and therefore of deposition rates, for films grown using various pH-adjusting solutions at various

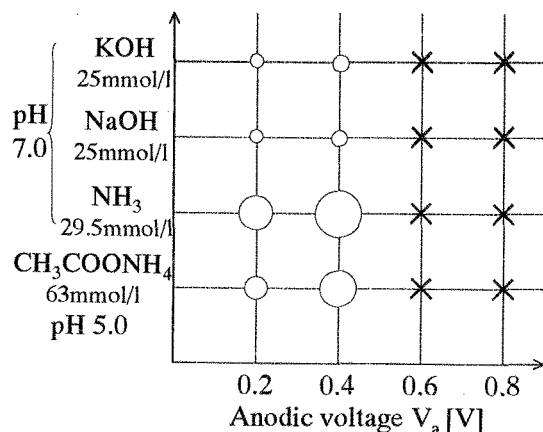


Fig.2 Phases in films synthesized on Cu substrates from aqueous solutions containing various pH-adjusting solutions; transverse axis shows anodic voltage applied on the substrates. Circles show single phase magnetite, bigger radius indicating stronger X-ray diffraction peaks. Crosses show mixed phase of $Fe_3O_4+FeOOH$.

values of V_a . At higher voltage, $V_a=0.6-0.8V$, mixed phase of ferrichydroxide $\gamma FeOOH$ appears, indicating that all Fe^{2+} ions are oxidized to Fe^{3+} , whereas Fe^{2+} are partially oxidized to Fe^{3+} in pure magnetite ($Fe^{2+}Fe^{3+}_2O_4$) which is obtained at lower V_a . The magnetite films deposited from $FeCl_2 + NH_3$ ($pH=7.0$) at $V_a=0.4V$ give the strongest X-ray scattering (Fig.2) and the highest deposition rate ($R_d=18.4nm/min$), as shown in Fig.3. They also give the best surface smoothness as revealed by SEM observation shown in Fig.4. All the films synthesized from the various reaction solutions at $V_a=0.4V$ have saturation magnetization of magnitude equal to that reported for bulk samples of Fe_3O_4 , within experimental error (Fig.3).

Next we fixed $V_a=0.4V$ and $C(FeCl_2)=30mmol/l$ and varied the concentration of NH_3 at $C(NH_3)=11.8-29.5mmol/l$. All the films obtained are single phase magnetite. Figure 5 shows that they have saturation magnetization of the same magnitude as bulk sample. The deposition rate (R_d) gradually increases with

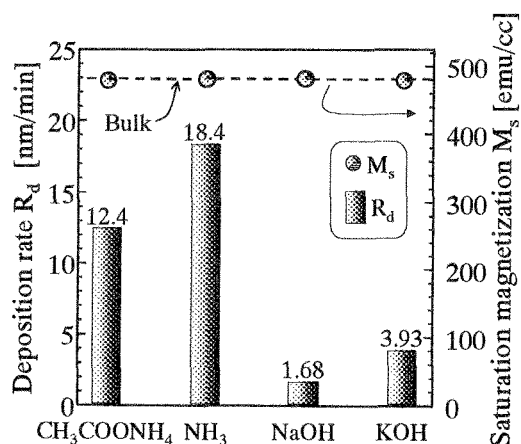


Fig.3 Deposition rate and saturation magnetization of magnetite films synthesized on NESA-glass substrates from aqueous solutions, and with an applied $V_a=0.4V$. The pH values and concentrations are as shown in Fig.2.

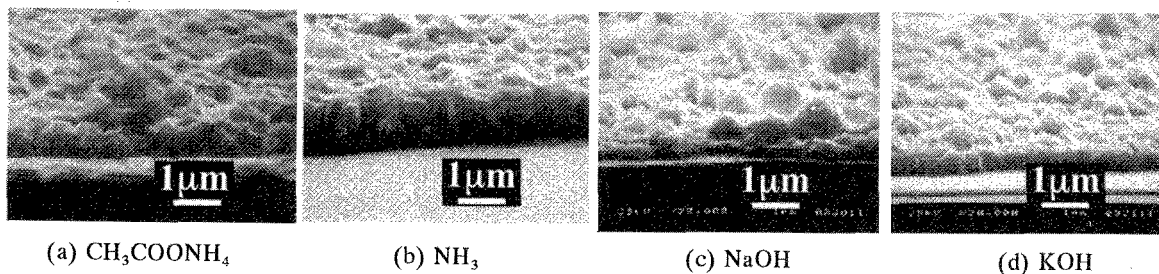


Fig.4 SEM observation on cross sections of magnetite films synthesized on NESA-glass substrates from aqueous solutions of pH values containing those pH-adjusting solutions and concentrations shown in Fig.2, applying $V_a=0.4$.

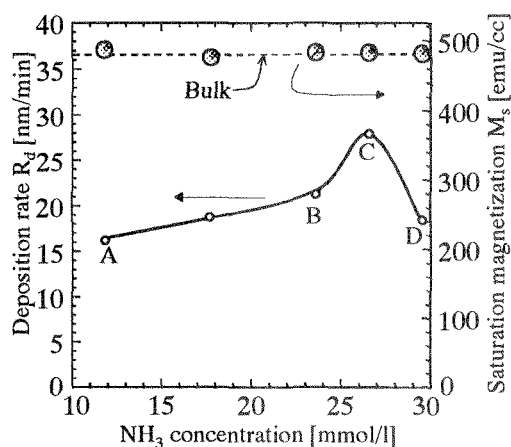


Fig.5 NH_3 concentration dependence of deposition rate and saturation magnetization of magnetite films which were synthesized from aqueous solution of FeCl_2 (30mmol/l) + NH_3 (11.8~29.5mmol/l), applying $V_a=0.4\text{V}$.

increasing $C(\text{NH}_3)$ which reaches a maximum value of 27.9nm/min at $C(\text{NH}_3)=26.6\text{mmol/l}$. This is because increase of R_d by increased oxidation activity at higher $C(\text{NH}_3)$ is offset by a partial precipitation of Fe^{2+} ions to $\text{Fe}(\text{OH})_2$, which was observed to occur when $C(\text{NH}_3)>29.5\text{mmol/l}$. The film designated as B in Fig.5, grown at relatively high deposition rate ($R_d=21.2\text{nm/min}$), is best in film quality having the smoothest surface

($\sim 0.3\mu\text{m}$ in average grain size), as shown in Fig.6.

4. CONCLUSION

By electro-ferrite plating using various pH-adjusting solutions, we prepared single phase magnetite films having saturation magnetization of the same magnitude as bulk sample. The best condition on which films of good surface smoothness are synthesized at relatively high deposition rate (27.9nm/min) is $V_a=0.4\text{V}$ and $C(\text{FeCl}_2)=30\text{mmol/l}$ + $C(\text{NH}_3)=23.6\text{mmol/l}$ and at $\text{pH}=6.9$.

ACKNOWLEDGMENT

This study has been financially supported by the "Research for the Future Program", from the Japan Society for the Promotion of Science, #JSPS-RFTF96R0691

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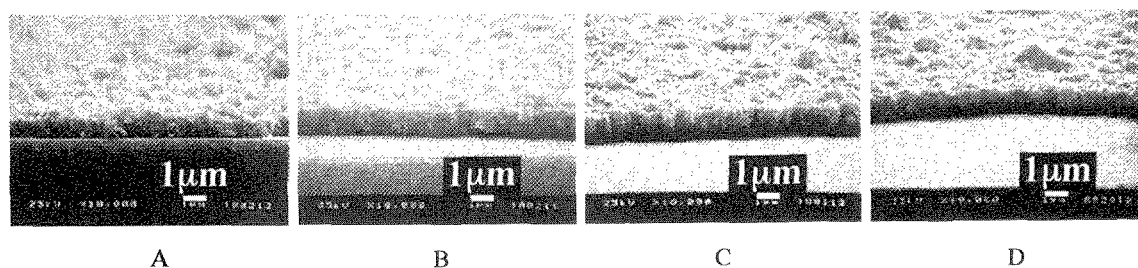


Fig.6 SEM observation on cross sections of magnetite films designated as A, B, C and D in Fig.5. Film on which D is taken is the same one on which (b) in Fig.4 is taken.

(Received February 4, 1999; accepted April 14, 1999)