Journal of ELECTRONIC MATERIALS
https://doi.org/10.1007/s11664-018-6764-x

5TH INTERNATIONAL CONFERENCE OF ASIAN UNION OF MAGNETICS SOCIETIES

High-Speed Electroplating of Fe Films Using DES-Based Plating Baths

TAKESHI YANAI,[1,2] TOMOKI YAMAGUCHI,[1] MASAKI NAKANO,[1] and HIROTOSHI FUKUNAGA[1]

1.—Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan. 2.—e-mail: t-yanai@nagasaki-u.ac.jp

We fabricated Fe films from deep eutectic solvent (DES)-based plating baths using constant direct current and investigated the effect of the current density and the bath concentration on the plating rate, magnetic properties and surface roughness of the Fe films. The plating rate increased with increasing the current density, and the maximum plating rate depended on the $FeCl_2$ concentration in the plating bath. The $FeCl_2$ concentration affected the surface roughness, and we confirmed that a high $FeCl_2$ concentration was effective in obtaining Fe films with smooth surfaces. Without deteriorations of the surface roughness or the soft magnetic properties, we consequently obtained a high plating rate value of approximately 930 μm/h by the increases in the current density and the $FeCl_2$ concentration. We, therefore, concluded that the DES is a promising solvents for high-speed plating of Fe films.

Key words: Electroplating, magnetic films, deep eutectic solvents

INTRODUCTION

Magnetic films are widely used in various electric devices and many fabrication processes, such as sputter depositions, vapor depositions, ion plating, and electroplating. To apply the films to commercial applications, a high deposition rate of the process is an important parameter, and some methods, e.g., pulsed laser deposition, aerosol deposition[1,2] and arc plasma deposition are well known as high-speed deposition processes.

Owing to high economic viabilities and high deposition rates, electroplating is one of the more effective methods to obtain magnetic films. Many studies on electroplated magnetic films have been carried out, and superior soft magnetic properties have been reported.[3–11]

Typical electroplating processes for soft magnetic films employ distilled water as the solvent for electroplating baths. Although aqueous solutions are suitable plating baths, it is difficult to deposit some metals due to decomposition of the water during the plating. Therefore, we recently introduced deep eutectic solvents (DES) for electroplating since many productive advantages of DES have been reported.[12–14] In our previous studies on soft magnetic films for DES-based plating baths, we found that the textures of electroplated Fe-Ni films dramatically changed depending on the Fe content in the film, confirming the high current efficiency of the plating process ($> 90\%$).[15–17] Since the current efficiency and the current density during the electroplating are particularly important parameters to obtain a high deposition rate, the obtained high current efficiency for the DES-based baths is attractive for realizing a high deposition rate. In the present study, we focused on another parameter of current density to enhance the

(Received July 17, 2018; accepted October 26, 2018)

Published online: 05 November 2018

deposition rate and investigated the effect of current density on the plating rate, the surface morphology and the magnetic properties of the Fe films.

EXPERIMENTAL

Electroplating

We have studied Fe-Ni-Co-system films in our previous studies and have confirmed the high current efficiency without depending on the film composition.[16] In this study, we electroplated Fe films to remove the effect of the film composition on the plating rate, the surface morphology, and the magnetic properties.

Amounts of 10 g of choline chloride ($HOCH_2CH_2N(CH_3)_3Cl$) and 10 g of ethylene glycol ($HOCH_2CH_2OH$) were stirred at 70°C to produce a DES, into which $FeCl_2{\cdot}4H_2O$ was added. Table I shows the bath composition. In this experiment, the bath concentration c_{bath} was defined by

$$c_{\mathrm{bath}} = \frac{x}{x + 20(\text{Weight of DES})} \times 100[\text{wt.\%}]. \qquad (1)$$

where x is the weight of $FeCl_2{\cdot}4H_2O$ in the bath.

An Fe plate and a Cu plate were used as the anode and cathode, respectively. The distance between the electrodes was set at 20 mm. The bath temperature was kept at 100°C, and no stirring action was undertaken during the plating. The films were electroplated using a direct current, and the current density and the plating time were controlled by a computer-aided current source (MATSUSADA, P4 K-80). Total charge was kept at 60 C. We consequently obtained 75-mm^2 Fe films on the 500-μm-thick Cu plate (Table II).

Measurements

We measured the thicknesses of the films at different 15 points with a micrometer (Mitutoyo, CPM15-25 MJ) and determined the thickness by averaging the measured values. The surface morphology and the surface roughness R_a were evaluated by a scanning electron microscope (SEM; Hitachi High-technologies, S-3000) and a surface roughness tester (Mitutoyo, SURFTEST SV-400), respectively. A VSM system (Tamagawa) was used for measurements of the hysteresis loops of the electroplated films (H_m = 1.6 MA/m) and the thermomagnetic curves. We determined the coercivity of the electroplated films from the hysteresis loops. The crystal structures of the films were analyzed by x-ray diffraction patterns (Rigaku, MiniFlex600).

Table I. Bath composition

Components	Weight (g)
$FeCl_2{\cdot}4H_2O$	x (10–33.3)
Choline chloride	10
Ethylene glycol	10

Table II. Electroplating conditions

Conditions	Value
Bath temperature T_{bath}	100°C
Current density j	0.1–2.5 A/cm^2
Plating time t_{plate}	800–32 s
Total charge Q	60 C

RESULTS AND DISCUSSION

Figure 1 shows the plating rates of the electroplating processes for the DES-based baths with various $FeCl_2$ concentrations as a function of the current density. The plating rates increased with increasing the current density, followed by a decrease in the higher current density. Since we employed a galvanostatic mode for the electroplating, the plating rate is proportional to the current density based on Faraday's law if the process has no loss for the reduction of the Fe ions in the bath. In the low current density region, the proportional increase in the plating rate could therefore be explained by Faraday's law. The decrease of the plating rate in the high current density region implies that the reduction of the Fe ions decreases. Since the maximum plating rate depended on the bath concentration, as shown in Fig. 1, the decrease in the plating rate is therefore due to a diffusion limitation of the Fe ions in the plating bath. This result suggests that the increases in the current density together with the bath concentration are effective in increasing the plating rate.

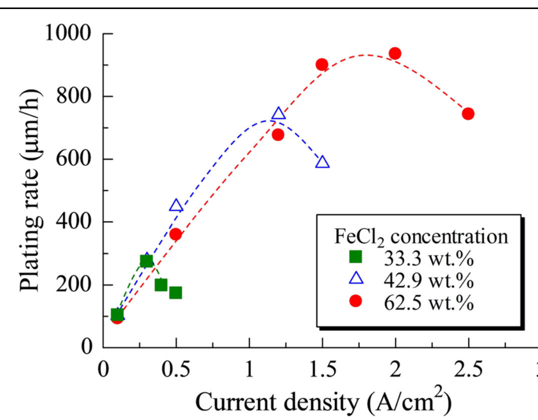

Fig. 1. Plating rates of the electroplating processes for the DES-based baths with various $FeCl_2$ concentrations as a function of the current density.

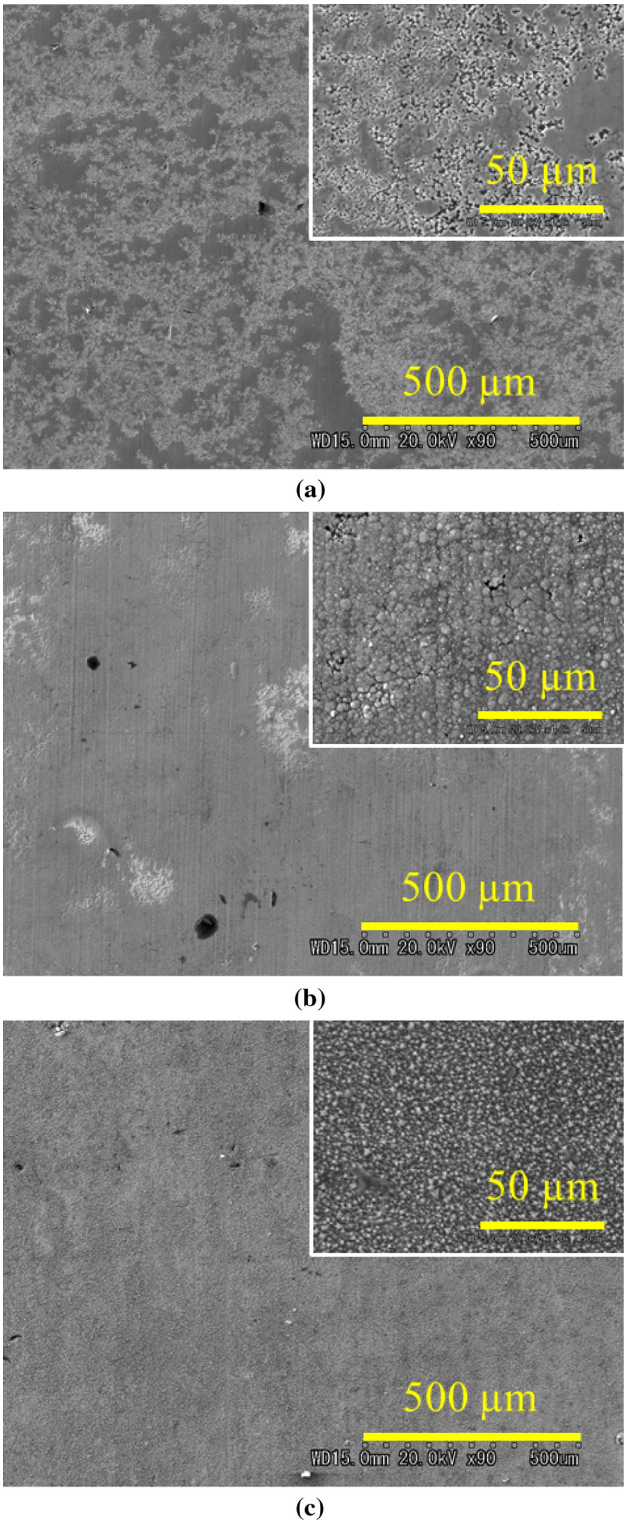

Fig. 2. SEM images of the Fe films plated in DES-based baths with various $FeCl_2$ concentrations of (a) c_{bath} = 33.3 wt.% (thickness: 23 μm), (b) c_{bath} = 42.9 wt.% (thickness: 21.5 μm), (c) c_{bath} = 62.5 wt.% (thickness: 20 μm). The current density was fixed at 0.1 A/cm^2.

For soft magnetic films, the surface roughness is one of the important factors for obtaining good soft magnetic properties. We, therefore, evaluated the surface conditions of the films. Figure 2 shows SEM images of the Fe films plated at various bath concentrations. Since we could not obtain high plating rates at the current density of 2 A/cm^2 for the baths with c_{bath}= 33.3 wt.% and 42.9 wt.%, the low current density of 0.1 A/cm^2 was employed in this experiment. As shown in Fig. 2, the surface roughness was slightly improved with increasing the bath concentration. Figure 3 shows SEM images of the Fe films plated at various current densities (c_{bath}= 62.5 wt.%). The rough surfaces were observed at a low current density, and the surface became smooth by increasing the current density. From the results in Figs. 2 and 3, we found that the current density and the bath concentration affected the surface roughness. To quantitatively evaluate the surface roughness, we measured the arithmetic average roughness, R_a. Figure 4 shows R_{a} as a function of the current density. The bath concentration changed the dependence of R_{a} on the current density. When the bath concentration is low, R_{a} increases with increasing current density. In contrast, R_{a} slightly decreases when the bath concentration is high, and the change in the R_{a} shows good agreement with the SEM images (Fig. 3). From the smooth surfaces and the high plating rates, we concluded that a plating bath with a high $FeCl_2$ concentration is effective in realizing high-speed plating of the Fe films.

Figure 5a shows the hysteresis loops of the Fe films plated at various current densities. The inset is an enlarged view of the magnetic saturation region. In this experiment, we used the plating baths with c_{bath}= 62.5 wt.% due to the solubility limit of the $FeCl_2$ in the DES. For typical magnetic films, since thickness is a factor in determining the magnetic properties, we controlled the thickness at 10 μm in this experiment. A slight difference in magnetic saturation was observed, and the films prepared at high current densities tended to reach the magnetic saturation quickly. To investigate this difference, we carried out thermomagnetic and XRD analyses. Figure 5b and c shows the thermomagnetic curves and XRD patterns of the Fe films, respectively. We obtained almost the same curves and patterns, indicating that the films do not have obvious structural differences. We, therefore, considered that the slight difference in the magnetic saturation to be attributed to the surface roughness.

From these results, we concluded that a DES bath with high $FeCl_2$ concentration is attractive for

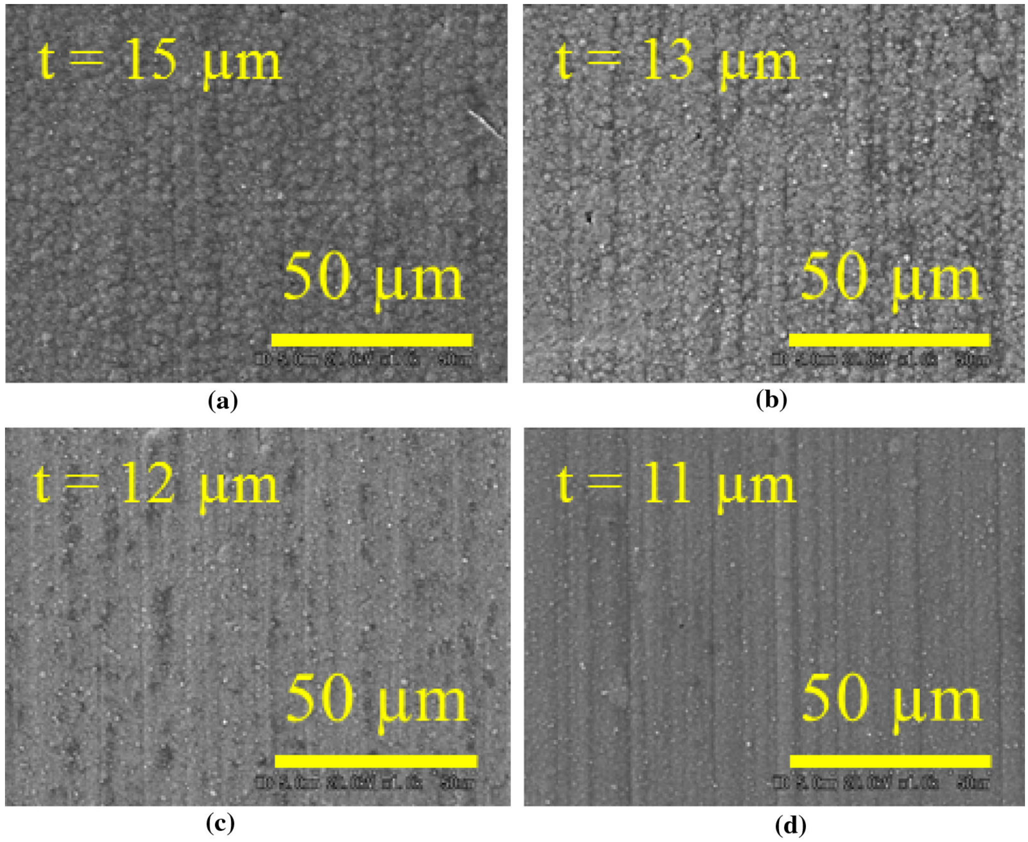

Fig. 3. SEM images of the Fe films plated at various current densities of (a) 0.5 A/cm^2, (b) 1.0 A/cm^2, (c) 1.5 A/cm^2, and (d) 2.0 A/cm^2. The $FeCl_2$ concentration was fixed at 62.5 wt.%.

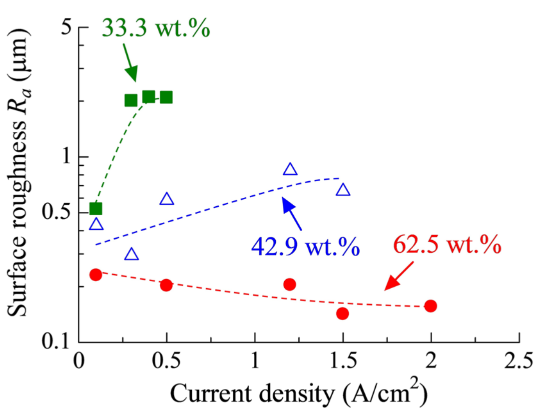

Fig. 4. The surface roughness R_a of the Fe films prepared from the DES-based baths with various $FeCl_2$ concentrations as a function of the current density.

realizing high-speed Fe plating. Consequently, we obtained a high plating rate value of approximately 930 μm/h.

CONCLUSION

We investigated the effects of the current density and bath concentration on the plating rates, the surface morphologies and the magnetic properties of Fe films prepared in the DES-based baths. The obtained results are summarized as follows:

(1) The plating rate of the Fe films increased with increasing the current density, and the maximum plating rate depended on the $FeCl_2$ concentration. These results imply that the limit of the maximum plating rate

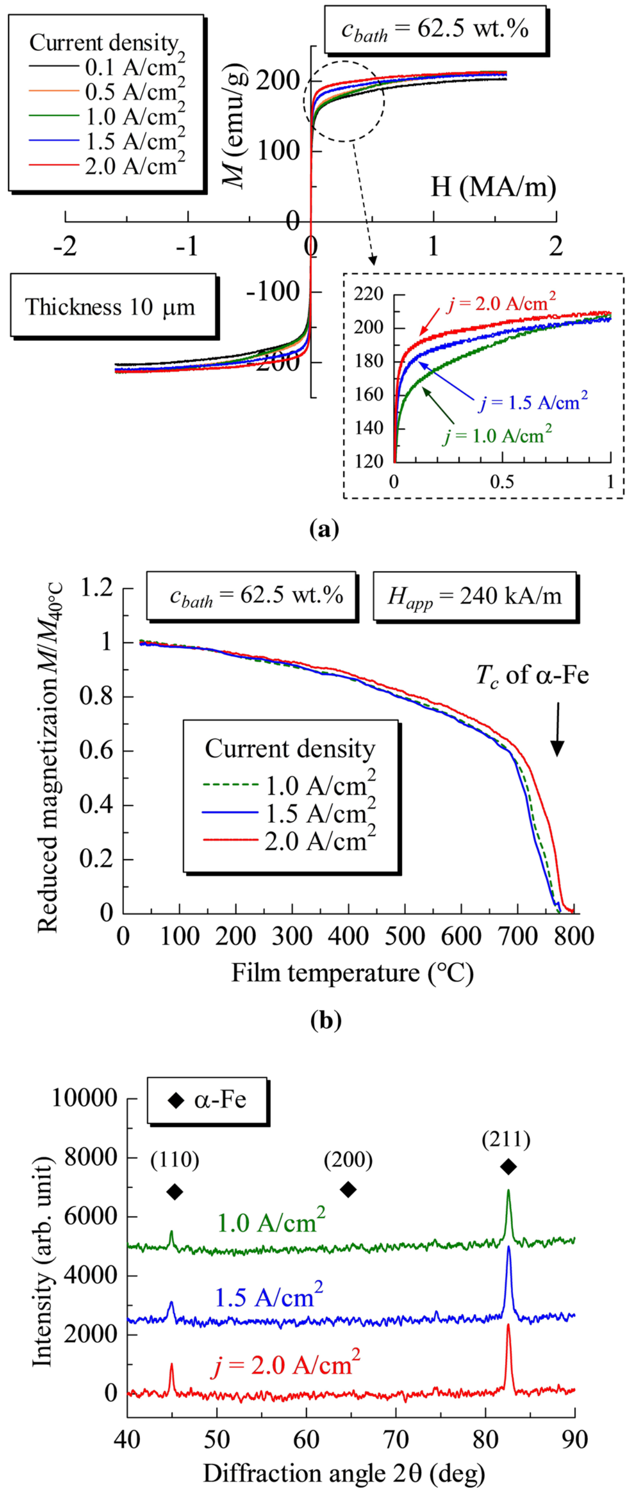

Fig. 5. (a) Hysteresis loops, (b) thermomagnetic curves, and (c) XRD patterns of the Fe films plated at various current densities. The magnetization in the thermomagnetic curves was reduced by the value at 40°C.

is determined by a diffusion limitation of the Fe ions.

(2) The current density and the bath concentration changed the surface morphologies of the Fe films. A high current density and high $FeCl_2$ concentration were effective in obtaining Fe films with smooth surfaces. In typical electroplating of metal films, high current density tends to promote crystal nucleation, and high metal ion concentration suppresses the diffusion limitation. We considered that these effects contributed to the improvement of the surface condition.

(3) Without apparent deteriorations of the magnetic properties, a high plating rate value of approximately 930 μm/h was obtained by the increase in the current density and the $FeCl_2$ concentration.

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