Electrodeposition of FeCoCd films with in-plane uniaxial magnetic anisotropy for microwave applications

Erxi Feng, Zhenkun Wang, Hongwei Du, Jinwu Wei, Derang Cao, Qingfang Liu,^{a)} and Jianbo Wang

Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Lanzhou 730000, People's Republic of China

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FeCoCd thin films with 500 nm thickness are directly prepared through electrodeposition in the sulphate bath in which glycine and citric acid were added as complex agents. The composition, structure, and magnetic of FeCoCd films were investigated as a function of Cd^{2+} concentration, cathode current density, and deposition temperature. A wonderful soft magnetic FeCoCd film was prepared and its coercivity of easy axis and hard axis are 5 Oe and 4 Oe, respectively. The natural resonance frequency is about 3.0 GHz, which imply that the FeCoCd film is potential candidate for high frequency applications. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4862094>]

I. INTRODUCTION

Recently, soft magnetic film materials are widely used in commercial devices due to their low cost and high integration, such as domestic microwave ovens, mobile phones, messaging apparatuses, as well as magnetic recording head.^{1,2} In addition, the frequency requirement for electromagnetic wave applications has reached several GHz-range.³ The soft magnetic thin films with in-plan uniaxial magnetic anisotropy can be applied in these areas.⁴ To achieve these soft magnetic films, electrodeposition techniques can be widely used because of its low capital cost, high deposition rate, and easy operation.^{5,6} Furthermore, the resistivity of the films prepared by electrodeposition is larger than those fabricated by sputtering because the electrodeposited film is constructed by incompactly stacked particles.^{5,7} The larger resistivity can resist the eddy current losses.

According to the Acher limitation,⁴ the higher $4\pi M_s$ is helpful to obtain higher μ_s and f_r . It is well known that $\text{Fe}_{100-x}\text{Co}_x$ alloys around $x=30$ own the highest $4\pi M_s$ of more than 2.4×10^4 Gs (2.45×10^4 Gs for the $\text{Fe}_{65}\text{Co}_{35}$ composition).⁸ However, the coercivity (H_c) of FeCo alloy films is so high (around 50–100 Oe) that they are not suitable for practical applications.⁵ One way to improve the soft magnetic properties of FeCo thin films is adding the third element to FeCo alloy films because suitable additives can reduce the grain size and lead to the low coercivity.⁹ A lot of FeCo based alloy films have been fabricated such as FeCoN, FeCoC, FeCoB, FeCoP, FeCoS, FeCoZr, and FeCoHf.^{6,10–15} But to our knowledge, there is few report on FeCoCd thin film. The possible reason is that it is difficult to obtain FeCoCd alloy by traditional methods due to the fact of the insolubility of the Fe-Cd or Co-Cd systems.¹⁶ In 1974, Narang *et al.* discussed the electrodeposition of FeCoCd alloy from the sulphate bath while the dextrin is in the bath.¹⁷ However, the addition of dextrin is harmful to obtain

thin FeCoCd films. And the magnetic properties of FeCoCd film are still missing.

In this work, FeCoCd thin films with 500 nm are directly prepared through electrodeposition when citric acid replaces dextrin in the sulphate bath. The composition, structure, and magnetic properties of FeCoCd films were investigated as a function of Cd^{2+} concentration, cathode current density, and deposition temperature.

II. EXPERIMENTAL

FeCoCd alloy films were electrodeposited from sulfate-based electrolytes onto ITO conductive glass substrates under the galvanostatic conditions. All the electrodepositions were performed in an electrochemical workstation (CHI 860D). The working electrode was ITO conductive glass, and the counter electrode was platinum sheet with an area of 4 cm^2 . A saturated calomel electrode (SCE) was employed as the reference electrode, and all potentials of our experiments were referred to the SCE. The contents of electrolyte together with operating conditions were shown in Table I.

The morphology and elemental composition were monitored by the scanning electron microscopy (SEM, Hitachi S-4800, Japan) combined with energy-dispersive X-ray spectrometry (EDS). The crystalline structure was studied by the X-ray diffraction technique with a Cu K_α radiation (XRD, Philips X'Pert, Holland). The magnetic properties were investigated using vibrating sample magnetometer (VSM, Lakeshore 7304, USA) and vector network analyzer (VNA, Agilent E8363B, USA) from 100 MHz to 5 GHz through a shorted microstrip transmission-line perturbation method.¹⁸

III. RESULTS AND DISCUSSION

The FeCoCd thin films were cost-effectively prepared via electrodeposition. The composition, micro-structure and magnetic properties of the films largely depending on the Cd^{2+} concentration, cathode current density as well as the deposition temperature.

^{a)}Author to whom correspondence should be addressed. Electronic mail: liuqf@lzu.edu.cn.

TABLE I. Electrolyte compositions and operating conditions.

Chemical/conditions	Concentration
FeSO ₄ ·7H ₂ O	0.1 mol/L
CoSO ₄ ·7H ₂ O	0.1 mol/L
CdCl ₂ · ⁵ / ₂ H ₂ O	0–0.008 mol/L
H ₃ BO ₃	0.5 mol/L
Citrate acid	2 g/L
L-ascorbic acid	1 g/L
Glycine	1 g/L
Saccharin	2 g/L
Lauryl sodium sulfate	0.2 g/L
Electrolyte pH	2.6
Bath temperature	20–50 °C
Operating time	140–300 s
Cathode current density	6.3–19.0 mA/cm ²

A. Effects of Cd²⁺ concentration in the bath

Different samples were electrodeposited from different Cd²⁺ concentration, when the cathode current density and deposition temperature were maintained at 6.3 mA/cm² and 20 °C, respectively. Fig. 1 shows composition and X-ray diffraction patterns of FeCoCd films under different Cd²⁺ concentration in the bath. It can be seen that the atomic ratio of Fe:Co remains at about 55:45. The Cd content in FeCoCd films increases from 0% to 12% at first then keeps unchanged with increase of Cd²⁺ ions concentration in the bath. When Cd²⁺ ions concentration is above 0.006 M, the transport agent reach to the full load due to the constant concentration of complexing agent in solution, thus, the Cd content remains unchanged. Fig. 1(b) shows the typical XRD patterns for FeCoCd films with different Cd contents. The main diffraction peak appears at $2\theta \approx 45^\circ$, which is corresponding with a bcc Fe-Co phase with a (110) diffraction. Another two diffraction peaks (200) and (211) gradually disappear with the Cd content increasing. The detail of main diffraction peak from 43° to 47° is clearly

FIG. 1. Composition (a) and X-ray diffraction patterns (b) for FeCoCd films prepared with various Cd²⁺ concentration.

displayed in the right inset. As the Cd content increases in FeCoCd films, the diffraction peak broadens and shifts to low diffraction angle. This is because the doping of Cd atoms improves the grain refining and, simultaneously, leads to the lattice expansion.

SEM images of FeCoCd films are shown in Fig. 2. It obviously exhibits the uniform grain distribution and decreasing grain size with the increase of Cd content, which is in accordance with the *FWHM* (Full Width at Half Maximum) of X-ray diffraction peak.

The inset in Fig. 3 shows that Cd doped FeCo alloy films have excellent soft magnetic performance and in-plane uniaxial anisotropy. The coercivity along the easy axis and hard axis are approximately 10 Oe and 3 Oe, respectively. It can be seen from Fig. 3 that when the Cd content in FeCoCd films increases, the doping of Cd atoms remarkably enhances the coupling between grains, which cause higher coercivity, and then grain size plays an important part in the decreasing of coercivity. Thus the coercivity increases at first then decreases with the increasing of Cd content. In-plane uniaxial anisotropy field has the same trend with the coercivity. Considering the lower coercivity and the higher anisotropy field of obtained

FIG. 2. SEM images of FeCoCd films (a)–(f) fabricated at different Cd²⁺ concentration. FIG. 3. The coercivities and anisotropy field vs. Cd²⁺ concentration, inset: The hysteresis loop of sample prepared at 0.003 mol/l Cd²⁺ concentration.

FeCoCd films, 0.003 M Cd^{2+} concentration is chosen as a suitable electrochemical condition in the following study.

B. Effects of current density and deposition temperature on FeCoCd films

Cathodic current density and deposition temperature are also important electrodeposition parameters. First, on the conditions of 0.003 M Cd^{2+} concentration and 20 °C deposition temperature, FeCoCd films were prepared at different cathodic current density. The composition, coercivity, and anisotropy field for films are listed in Table II. It can be seen that high uniaxial anisotropy field is obtained at higher current density, meanwhile the easy axis coercivity H_{ce} also increases with the increase of current density. So, a relatively appropriate current density 12.7 mA/cm² is selected in consideration of practical applications. Second, different samples were electrodeposited at different deposition temperature and other selected conditions (0.003 M Cd^{2+} concentration and 12.7 mA/cm² cathodic current density). Table III clearly exhibits that as the deposition temperature rises, the coercivity along easy axis decreases (11 Oe–5 Oe), and the anisotropy field gradually increases (44 Oe–52 Oe).

Finally, the optimum conditions (0.003 M Cd^{2+} concentration, 12.7 mA/cm² cathodic current density, and 50 °C deposit temperature) are found to prepare FeCoCd film with low coercivity and relatively larger anisotropy. Fig. 4(a) shows the hysteresis loop of the FeCoCd film fabricated under the optimum conditions, and complex permeability spectra is shown in Fig. 4(b). The coercivity along easy axis is only 5 Oe, and anisotropy field can reach to 52 Oe. The natural ferromagnetic resonance frequency is approximately 3 GHz. The permeability spectra can be analyzed based on the Landua–Lifshitz–Gilbert (LLG) equation as follows:

TABLE II. Composition and magnetic properties for FeCoCd films under the varies current density.

EDS (at. %)/VSM	Current density(mA/cm ²)				
	6.3	9.5	12.7	15.9	19.0
Fe %	48	49.9	50.9	51.5	51.3
Co %	45.9	46.9	46.6	45.9	46.6
Cd %	6.1	3.2	2.5	2.6	2.1
H_{ce} (Oe)	8.4	9.8	10.5	11.5	12
H_{ch} (Oe)	3.6	3.9	3	2.5	4
H_k (Oe)	37	42	45	49	49

TABLE III. Composition and magnetic properties for FeCoCd films under the different deposition temperature.

EDS (at. %)/VSM	Deposition temperature (°C)			
	20	30	40	50
Fe %	50.9	50.6	47.7	41.8
Co %	46.6	46.8	48.8	53.6
Cd %	2.5	2.6	3.5	4.6
H_{ce} (Oe)	10.5	8.5	6.5	5.3
H_{ch} (Oe)	3	3.2	2.5	4.5
H_k (Oe)	45	49	49	51

FIG. 4. The hysteresis loop (a) and complex permeability (b) for the film fabricated at the optimum conditions, the solid lines in Fig 4(b) are fits to the LLG equation with the damping parameter of 0.05, the saturation magnetization of 13850 Gs and the anisotropy field of 56 Oe.

$$\mu(f) = 1 + \frac{\gamma^2 4\pi M_s (4\pi M_s + H_k) + j\gamma\alpha f 4\pi M_s}{\gamma^2 4\pi M_s H_k - (1 + \alpha^2)f^2 + j\gamma\alpha f (4\pi M_s + 2H_k)},$$

where, γ is the gyromagnetic ratio, $4\pi M_s$ the saturation magnetization, and α the damping parameter. It can be observed that experimental values and resonance frequency are in good agreement with the theoretical analysis result when the damping parameter for this film is assumed to be $\alpha = 0.05$, the saturation magnetization is 13850 Gs, and the anisotropy field is 56 Oe.

IV. CONCLUSION

FeCoCd alloy films were successfully prepared by electrodeposition technique, and the effects of Cd^{2+} concentration, cathodic current density and deposit temperature on composition, structure, and magnetic properties were investigated. On the conditions of 0.003 M Cd^{2+} concentration, 12.7 mA/cm² cathodic current density and 50 °C deposit temperature, the $\text{Fe}_{42}\text{Co}_{53}\text{Cd}_5$ film possessing excellent soft magnetic properties was fabricated. The natural ferromagnetic resonance frequency is approximately 3 GHz, which imply that the FeCoCd film is potential candidate for high frequency applications.

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