Research Letter

Ultrasoft and High Magnetic Moment CoFe Films Directly Electrodeposited from a B-Reducer Contained Solution

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A methodology to fabricate ultrasoft CoFe nano-/microfilms directly via electrodeposition from a semineutral iron sulfate solution is demonstrated. Using boron-reducer as the additive, the CoFe films become very soft with high magnetic moment. Typically, the film coercivity in the easy and hard axes is 6.5 and 2.5 Oersted, respectively, with a saturation polarization up to an average of 2.45 Tesla. Despite the softness, these shining and smooth films still display a high-anisotropic field of ~ 45 Oersted with permeability up to 10^4 . This kind of films can potentially be used in current and future magnetic recording systems as well as microelectronic and biotechnological devices.

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1. INTRODUCTION

The ever expanding demand of the world market leads to magnetic recording data storage devices advancing toward much smaller exterior dimension and higher capacity [1, 2]. In order to achieve very high capacity and fast recording data storage in a miniature device, an ultrasoft and high magnetic moment material is required for producing high-saturation flux density (B_s), so that the necessary flux density can be preserved on reducing device dimensions, while simultaneously achieving a low coercivity (H_c) to match the hard magnetic media with high H_c , track density, and linear density [3]. Soft magnetic films with high moment are also widely used in modern electromagnetic devices, such as high-frequency field-amplifying components, versatile communication tools, and magnetic shielding materials in tuners [4]. Although numerous soft or high- B_s magnetic films have been achieved nowadays via sputtering, evaporation, and casting, most of them cannot be applied to device fabrication due to the following reasons: low-deposition rate (usually $< 8 \text{ Å/s}$) and high-internal stress films from sputtering [5], overly thick films (commonly $> 1 \text{ mm}$) from casting, and coarse-grained films from evaporation [6]. In addition, most of the reported materials have limited B_s of $\leq 2.1 \text{ T}$ (e.g., NiFe, FeCoNi films) [3]. Despite CoFe alloy possessing the highest B_s of about 2.45 T theoretically, the

CoFe nano/microfilms prepared always encounter two vital issues for application: poor magnetic properties [such as poor anisotropy, high value of H_c (always $> 4 \text{ Oe}$)] and poor mechanical properties (such as rough surface, and cracking film) [7]. Electrodeposition is a fast and simple method to achieve various thicknesses of soft Fe-based materials with lower stress [8, 9]. However, preventing Fe^{2+} from oxidization into Fe^{3+} (which decreases B_s), and minimizing the H_c and roughness of the metal films are challenges in electrodeposition [3, 7]. So far, only the softest magnetic CoFe film, which possesses an easy axis H_c (H_{ce}) and hard axis H_c (H_{ch}) of 15 and 4.8 Oe, respectively, has been reported [7].

Herein, we demonstrate a novel approach to the fabrication of ultrasoft magnetic CoFe films via electrodeposition from a sulfate salt-based solution containing dimethylamine borane $[(\text{CH}_3)_2\text{NHBH}_3]$ (B-reducer, Bayer AG, Germany). In comparison with commonly used strong acidic solutions (corroding devices) which contain S-additives (saccharin, Na Lauryl sulfate), the solution containing B-reducer is a semineutral medium with larger process latitude. For instance, the pH range (3.5–5.1) is much wider than that of the common plating solutions containing S-additives (pH = 2.3–2.5 or 2.5–3.0) [7, 9]. Furthermore, the plating solution does not require a salt bridge to protect Fe^{2+} from oxidization. The thickness of the prepared films measured

TABLE 1: Property comparison of CoFe films (without annealing).

Property	No additive	B-reducer (1.5 g/L)	B-reducer (3 g/L)	S-additive ⁷
H_{ce} (Oe)	63	6.6	6.5	13
H_{ch} (Oe)	53	5.8	2.5	4.8
H_k (Oe)	78	26	45	20.2
μ_m	7.8×10^1	4.5×10^4	5.8×10^4	—
B_s (T)	1.42	2.31	2.45	2.45

through atomic force microscopy (AFM) ranges from tens of nanometers to micrometers. The magnetic characterizations performed by using vibrating sample magnetometer (VSM) and superconducting quantum interference device (SQUID) show that the films are very soft magnets with good anisotropy and high magnetic moment properties.

2. METHOD AND RESULTS

The CoFe films were electrodeposited on Si(100) wafers. A seed layer, for example, Au, Cu, or CoFe, with thickness of 20–30 nm was sputtered onto each wafer surface as an electrical conducting layer for the electrodeposition. The $\text{Fe}_x\text{Co}_{100-x}$ ($x = 55\text{--}68$) films were fabricated at the temperature of $40 \pm 2^\circ\text{C}$ from a solution of 0.07 mol/L $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 0.10 mol/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 mol/L NH_4Cl , 0.5 mol/L H_3BO_3 , and 2.8–3.2 g/L B-reducer additive. The electroplating system used was a Paddle cell with pulse DC power. During the electrodeposition of CoFe film, a magnetic field of 280 Oe was applied parallel to the substrate surface. The atomic ratio of Co to Fe in the electrodeposited films was determined by energy dispersive X-ray (EDX, JSM-6340F, JEOL Asia). While measuring H_c with the VSM possessing Helmholtz coils, high resolution of 0.01 Oe was obtained through the field control mode. The maximum relative permeability (μ_m) was calculated from easy axis M - H loops according to the formula $\mu_m = B(T)/H(T) \approx 4\pi$ magnetic moment (M , emu)/[magnetic field (H , Oe) $\times$ film volume (cm^3)], where (M, H) refers to the turning point in the lower branch of the easy axis M - H loop. It is noted that the effect of film sample shape (normally, $1.20 \text{ cm} \times 1.20 \text{ cm} \times \sim 0.6 \mu\text{m}$) can be neglected due to the length and width being much larger than the thickness [10, 11]. The B_s values were calculated from the formula $B_s(T) = \mu_0 M_s = 4\pi \times 10^4 M$ (emu)/film volume (cm^3), where M refers to the saturation moment in the M - H loops. The B_s result is the average value obtained from a series of CoFe films having different thickness (80 nm – 2.5 μm). The dimension of the films was measured on ADM-60 Micro-Dicer. The total error of B_s measurement is 0.01 T.

Table 1 shows that the B-reducer dramatically induces the decrease of H_c and the increase of B_s with its addition increasing from 0 to 100 mL/L. It is due to the fact that despite the absence of salt bridge (leading to a lower efficiency of plating current) to prevent Fe^{2+} from oxidation in the solution, the B-reducer can protect the as-synthesized CoFe film effectively from oxidation since B-reducer, acting

FIGURE 1: The M - H loops of the $\text{Co}_{40}\text{Fe}_{60}$ films electrodeposited (at a current density of $\sim 6.0 \text{ mA/cm}^2$) from the solutions which contain B-reducer of (a) 0.0, (b) 1.5, and (c) 3.0 g/L, respectively.

as a reductant molecule, can reduce Fe^{3+} (produced during plating) back into Fe^{2+} :

Despite the addition, the B-reducer did not lead to too much boron doping into the CoFe film. Hence, there is a very low content of oxygen and boron present in the deposited CoFe films, in which the low oxygen content

FIGURE 2: The AFM and FESEM (inset) images of the $\text{Co}_{40}\text{Fe}_{60}$ films electrodeposited (at a current density of $\sim 6 \text{ mA/cm}^2$) from the solutions which contain B-reducer of (a) 0, (b) 1.5, and (c) 3.0 g/L, respectively. The scale bar in the inset (a)–(c) is 1 μm , 100, and 100 nm, respectively.

cannot be detected by EDX, while the boron content is less than 0.8% after XPS analyzing. For the $\text{Co}_{40}\text{Fe}_{60}$ film deposited from a current density of 6.0 mA/cm^2 , with the concentration of B-reducer increasing from 0.0 to 3.0 g/L in the electroplating solution, the H_{ce} and H_{ch} values decrease from 63 and 53 to 6.5 and 2.5 Oe, respectively, while B_s increases from 1.4 to 2.45T in average. On the other hand, the permeability (μ_m) of CoFe film also increases from the order of 10^1 to 10^4 after the addition of B-reducer. Thus, the film becomes very soft due to the effect of B-reducer. Figure 1 shows the magnetic moment–applied field curves (M-H loops) of the CoFe films from the solutions containing different concentrations of B-reducer. It appears that the loops along the easy and hard axes change from being similar [such as in Figure 1(a)] to distinctly different [shown in Figure 1(c)]. Hence, the ultrasoft and high magnetic moment of $\text{Co}_{40}\text{Fe}_{60}$ film possess a much larger anisotropy compared to the softest CoFe films reported to date [7]. Further investigations revealed that although similar effects of B-reducer had also been observed for other components of CoFe films by varying the plating current density, only the films with formulas from $\text{Co}_{35}\text{Fe}_{65}$ to $\text{Co}_{43}\text{Fe}_{57}$ could achieve a high B_s of $\geq 2.4T$, and such films were electrodeposited at a current density ranging between 4.8 and 7.2 mA/cm^2 .

More measurements were carried out to identify the mechanism for the effect of B-reducer on the properties of CoFe films. In Figure 2, the AFM and FESEM images show the surface variations of the deposited $\text{Co}_{40}\text{Fe}_{60}$ films with the increase of B-reducer concentration from 0 to 1.5, then to 3.0 g/L. The sizes of CoFe nanoparticles become much smaller (roughly from 80 to 10–30 nm) with the increase of B-reducer concentration in the electroplating solution. Thus, for the films, H_c drops and μ_m increases drastically since the average magnetocrystalline anisotropy and the exchange coupling range become lower and wider, respectively, with the smaller ferromagnetic nanoparticles [10, 11]. In addition, X-ray diffraction (XRD) analysis (recorded from a powder sample) in Figure 3 shows that the added B-reducer eliminates the foreign Fe_2O_3 -phase (viz. protects Fe^{2+} from oxidation), which leads to a texture-structural change from CoFe(110) and Fe_2O_3 (209) polycrystalline to CoFe(110) single-crystalline for the $\text{Co}_{40}\text{Fe}_{60}$ films. As a result, the film possesses very low H_c [11] and high theoretical B_s value ($\sim 2.45T$) [7]. Further investigation results revealed that too much of B-reducer ($>10 \text{ g/L}$) led to an unstable plating solution and a high content of boron doping ($>2\%$) in the CoFe films. The films possess an amorphous texture, a decreased B_s , and poor anisotropy.

Apart from having excellent magnetic properties, our characterizations shown in Table 2 indicate that the CoFe films also displayed good mechanical and other properties, such as very low magnetostriction (λ_s) and surface roughness (R_a , also depicted in Figure 1), and absence of microcracking defects, which is a critical problem faced by current CoFe electrodeposition [7, 12]. These properties also contribute to low H_c of the films [10].

TABLE 2: Properties of soft $\text{Co}_{40}\text{Fe}_{60}$ films.

Film	H_{ce} (Oe)	H_{ch} (Oe)	B_s (T)	λ_s ($\times 10^{-6}$)	Surface	R_a (nm)
Before anneal	6.5	2.5	2.45	9.2	Shining	2.4
After anneal	5.6	1.8	2.43	3.4	Shining	2.2

Note: the annealing was conducted at 200°C for 4 hours.

FIGURE 3: The 2θ XRD results of $\sim 0.6 \mu\text{m}$ $\text{Co}_{40}\text{Fe}_{60}$ films on Si(100) wafer. (a) and (b) stand for without adding and adding B-reducer, respectively.

3. CONCLUSION

The two challenging issues (poor magnetic and mechanical properties), encountered in the preparation of high- B_s magnetic CoFe films [7], can simply be solved by using boron reducer in electrodeposition. The boron reducer can greatly improve the softness, magnetic moment, mechanical, and other properties of the CoFe films. Thus, the as-prepared films have potential applications in ultrahigh density and frequency magnetic recording system, biotechnological, and microelectronic devices [2, 4].

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