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Short Communication

Compositional and Structural Analysis of FeCo Films Electrodeposited at Different Temperatures

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In this paper, the effect of electrodepositing temperature on the composition and microstructure of FeCo films were investigated in details. At low temperature (less than 40 °C) Fe is preferentially deposited. With increasing temperature, the Co content is increased while Fe content is decreased. The film grown at RT has a mixed phase (fcc + bcc), but the films deposited at 30 °C and 40 °C show only bcc phase. When the electrodeposition temperature is increased to 50 °C, a metastable α-Mn phase becomes dominant and bcc phase is relatively less in the Fe Co film. Further increasing the temperature to 60 °C, the film has a mixed phase of α-Mn phase and hcp Co phase. It can be concluded that elevated electrodeposition temperature promotes the formation of metastable α-Mn phase while the fcc solid solution forms at low temperature. The bcc α-Co_7Fe_3 phase is favored at intermediated temperature. FeCo films with mixed phases have a finer grain size than that of the films with single phase due to the competitive growth of grains in the mixed phase.

Keywords: FeCo film; electrochemical deposition

1. INTRODUCTION

FeCo alloys have been extensively studied as soft magnetic materials due to their good properties. They have been used widely and commercially in magnetic sensors, magnetic recording head, motors, and generators in electric vehicles since it has high Curie temperature, high magnetization, low coercivity, low hysteresis loss, low eddy current loss, high electric permeability and good thermal stability.[1~3]

Although numerous soft or hard magnetic films are being fabricated via sputtering, evaporation and molecular beam epitaxy (MBE) techniques, most of them require high or high vacuum and cannot be applied to device fabrication due to low deposition rate and high costs. It is also possible to grow such ferromagnetic films with high quality by electrodeposition, which does not need any vacuum system. Electrodeposition of FeCo alloy films is one of the most popular fabrication processes for its low cost and simple, flexible operation, inexpensive apparatus and easy reliable control by changing the parameters in the whole electrodeposition process although stable plating baths are needed for commercial processing. Moreover, it is generally compatible with the fabrication of magnetic components with irregular shapes in integrated devices [4].

In electrodeposition, the growth mechanism, morphology and microstructure and physical properties of the films depend on electrodeposition conditions such as electrolyte pH, temperature, deposition potential and electrolyte composition. The deposition temperature was observed to change significantly the microstructure, morphology and magnetic properties of electrodeposited films [5, 6]. It is well known that the magnetic properties of Fe-Co films are greatly affected by their compositions and microstructures [1~3], thus a reliable control of the composition and microstructure is an important issue in designing the magnetic functionality of these materials.

In present study, the composition and microstructure of electrodeposited Fe-Co films were investigated as a function of the deposition temperature in bath. It was observed that the composition and microstructure were changed significantly with the deposition temperature.

2. EXPERIMENTAL

FeCo thin films were fabricated by electrodeposition from Sulfate bath using a conventional three electrode cell. The copper plate serves as the working cathode with the surface area of 1cm^2 while a graphite plate serves as the anode with much larger surface area. Prior to deposition, the substrate was first mechanically polished, then washed in 10% H_2SO_4 and distilled water. The reference electrode was a saturated calomel electrode.

Table 1. Compositions of the electrolytes and major electrodepositing parameters

Composition	pH	Current density (mA/cm^2)
$CoSO_4.7H_2O$ (0.2mol/L) $FeSO_4.7H_2O$ (0.15mol/L) Na_2SO_4 (0.7mol/L) Ascorbic Acid (0.05mol/L) Boric acid (0.4mol/L)	3	10

The compositions of the electrolytes of Co^{2+}/Fe^{2+} were shown in Table 1, together with major electrodepositing parameters. The total concentration of ferrous sulfate [$FeSO_4 \cdot 7H_2O$] and cobalt sulfate [$CoSO_4 \cdot 7H_2O$] was kept 0.35 mol/L. All chemicals were reagent grade and dissolved in distilled water. The electrodeposition was conducted at different operating temperatures (room temperature to 60°C) with a certain stirring rate.

The crystallographic structure of electrodeposited FeCo films was characterized by X-ray Diffraction (XRD). The compositions of the samples were detected through energy dispersive spectrometer (EDS).

3. RESULTS AND DISCUSSION

The molar ratio of Co:Fe in the bath solution was 4:3, which should result in electrodeposited films with compositions of ~57 at% Co (~43 at% Fe) assuming non-preferential electrodeposition. The compositions of electrodeposited Co–Fe thin films are shown in Fig.1.

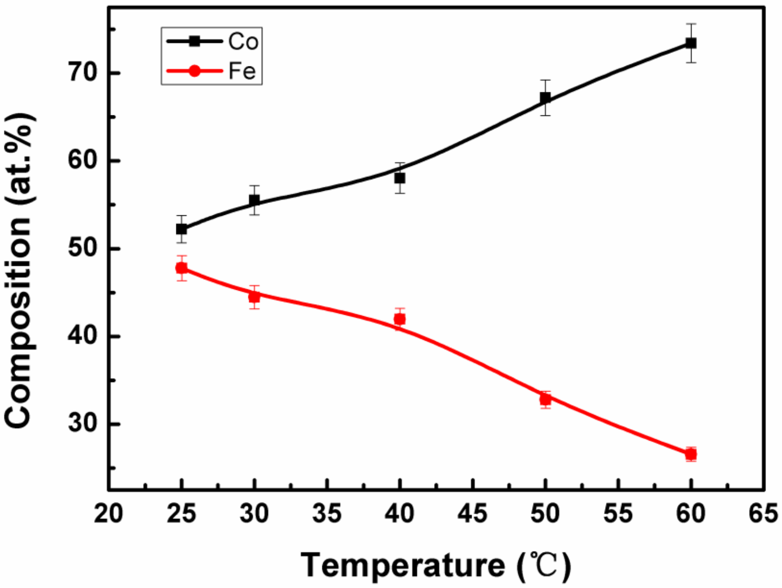

Figure 1. Compositions of Co–Fe thin films electrodeposited at different temperatures

As can be seen, at room temperature, Fe is preferentially deposited, relative to the composition of electrolyte solution, at the expense of Co. Iron has a lower reduction potential than Cobalt. Therefore, the results indicate slightly anomalous electrodepositing behavior for the electrolyte solution at room temperature. This behavior is well established in previous studies [7-9] and is thought to be the result of an inhibiting effect of Fe on the nucleation and growth of Co on the cathode surface [9]. When the depositing temperature is increased to 40 ^{o}C, the composition of the deposits closely reflects the solution composition, while at 60 ^{o}C the deposited films become Co-rich. At high temperatures (e.g., 60 ^{o}C), the behavior is as normally expected since the more noble metal (Co) is deposited preferentially; as a result, electrodeposited films contain more Co than the electrolyte composition.

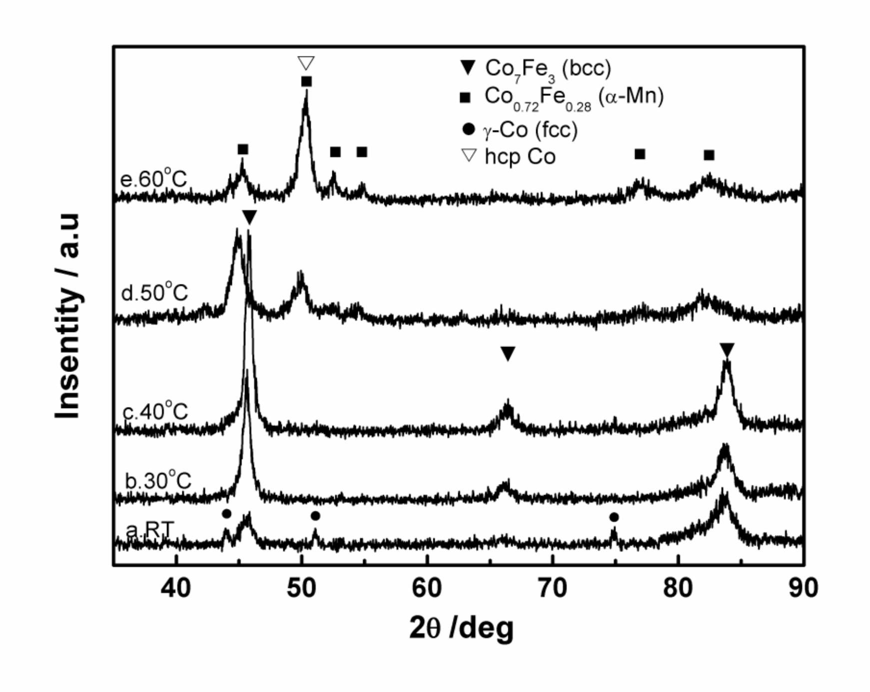

Figure 2. XRD patterns of FeCo films electrodeposited at different temperatures

Fig.2 shows the XRD patterns of FeCo films electrodeposited at different temperatures. From the patterns, it can be seen that the films have a mixed phases of face-centered cubic (fcc) solid solution (γ phase), body-centered cubic (bcc) α-Co_7Fe_3 phase (α-Fe type), $Co_{0.72}Fe_{0.28}$ phase with α-Mn structure and hcp Co phase. As seen from the figure, the reflections from the characteristic (111), (200) and (220) crystal planes of fcc CoFe solid solution phase were observed at approximately $2\theta=44^{o}$, 51^{o} and 75^{o}, respectively. In addition, the (110), (200), (211) peaks of bcc α-Co_7Fe_3 phase were observed at about 45^{o}, 66^{o} and 84^{o}, respectively. The patterns indicate that the film electrodeposited at room temperature (RT) has a mixed phase of fcc and bcc phases but the bcc phase is dominant. As the deposition temperature increases, the fcc phase transforms to bcc phase and the characteristic peaks of fcc phase disappear at the deposition temperature of 30 ^{o}C. The structure becomes completely bcc for the films deposited at 30 and 40 ℃ as seen from Fig. 2. As the electrodepositing temperature is increased to 50 ^{o}C, the characteristic peaks of metastable α-Mn type $Co_{0.72}Fe_{0.28}$ phase is detected strongly at peak positions of 44°,50°,52°,55°,76°and 81° while the peaks of bcc solid solution phase become very weak. When the temperature is increased further to 60 ^{o}C, the bcc solid solution phase disappears completely and (101) peak of hcp Co phase is observed beside the peaks of α-Mn type phase. Also, the relative peak intensity of α-Mn phase decreases when the bath temperature is increased to 60 ^{o}C. Results indicate that the fcc and bcc FeCo solid solutions form at lower temperatures and low Co concentrations while the metastable α-Mn phase is favored at high temperature and high Co concentrations. A two-phase mixed structure of the α-Mn phase and the bcc solid solution phase forms for intermediate conditions (50 ^{o}C). In addition, the formation of hcp Co phase can be explained as following: with increasing bath temperature, the concentration of Co increases up to about 74 at.%; during deposition, part of the Co ion is co-deposited with Fe ion to form α-Mn phase and other part of Co ion forms the hcp Co phase.

According to the phase diagram of Fe-Co binary alloy [10], fcc solid solution phase is thermodynamically stable for high Co concentration (>90 at%) at low temperature (<700 °C) or for all alloy concentrations at temperatures between ~985 °C and ~1475 °C while bcc α phase is stable for Fe concentrations in excess of 80 at% at temperatures below 500 °C. The binary phase diagram gives a good indication of the phases that might be expected in Fe–Co thin films at a particular composition. However, although thermodynamically stable at low temperature and over a wide composition range (25~75 at% Fe) according to the phase diagram (Fig. 1), the α' phase is never observed in our electrodeposited thin films and other researches [1-3, 11, 12]. It is reported [1-3, 11, 12] that under many electrodepositing conditions the fcc Fe-Co solid solution phase and bcc α phase form during electrodeposition. The formation of non-equilibrium phases of the two solid solution phases is not surprising for electrodeposition systems as the deposition rates do not provide sufficient time for the ordering of Co and Fe atoms on specific lattice positions to form α'-CoFe phase. In our work, for electrodeposition of FeCo films with Co concentrations ranging from around 50 to 75 at% at all bath temperatures, the fcc solid solution was only detected for the bath temperature of RT while the bcc phase was obtained for bath temperature from RT to 50 °C.

The metastable $Co_{0.72}Fe_{0.28}$ phase formed at elevated bath temperatures (50~60 °C). It was identified as a complex cubic phase (58 atoms per unit cell) which is isostructural to α-Mn (space group I-43m) [13]. The α-Mn type phase has previously been reported in FeCo alloys through precipitation reactions [14–17] and vapour deposition [15]. Phases with similar structures were also formed in Fe–Cr and Fe–Ni–Cr alloys through magnetron sputtering [18, 19]. As mentioned above, increased electrodepositing bath temperatures result in increased depositing Co contents. Therefore, an obvious question may be raised: whether the formation of the α-Mn type phase is the result of high Co contents in the films or the increase of electrodepositing temperatures. According to Zhou et al. [8], the formation of the α-Mn type phase is temperature dependent, and not composition dependent, as the α-Mn type formed at 40 and 60 °C in their deposited films containing 36–85 at% Co. The electrodeposited films studied in present experiment fall all within this composition range (Fig.1), but no α-Mn type phase formed at low temperatures (RT~40 °C), consistent with the results of Zhou et al. [8].

Table 2. Average lattice parameters (nm) of bcc phase and α-Mn phase in FeCo films electrodeposited at different temperatures

Temperature/ °C phase	RT	30	40	50	60
bcc phase	0.2830	0.2812	0.2805	-	-
α-Mn phase	-	-	-	0.8544	0.8522

The lattice parameters of the electrodeposited phase in films were calculated based on the peak positions in the XRD patterns. Table.2 shows the average lattice parameters of bcc phase and α-Mn phase in alloy films prepared at different bath temperatures. Higher depositing temperature leads to a small decrease in the lattice parameter for the bcc phase. This is to be expected due to the slightly smaller atomic radius of the Co atoms and enrichment of Co content in bcc phase. The incorporation of small atoms into the lattice of the film would shrink the lattice and decrease the lattice parameters. The lattice parameter of the α-Mn phase also slightly decreases when the depositing temperature is increased. This may indicate a slight enrichment of Co in the α-Mn phase of film electrodeposited at 60 ^{o}C relative to that of film electrodeposited at 50 ^{o}C. This results in a reduction in the lattice parameter of α-Mn phase.

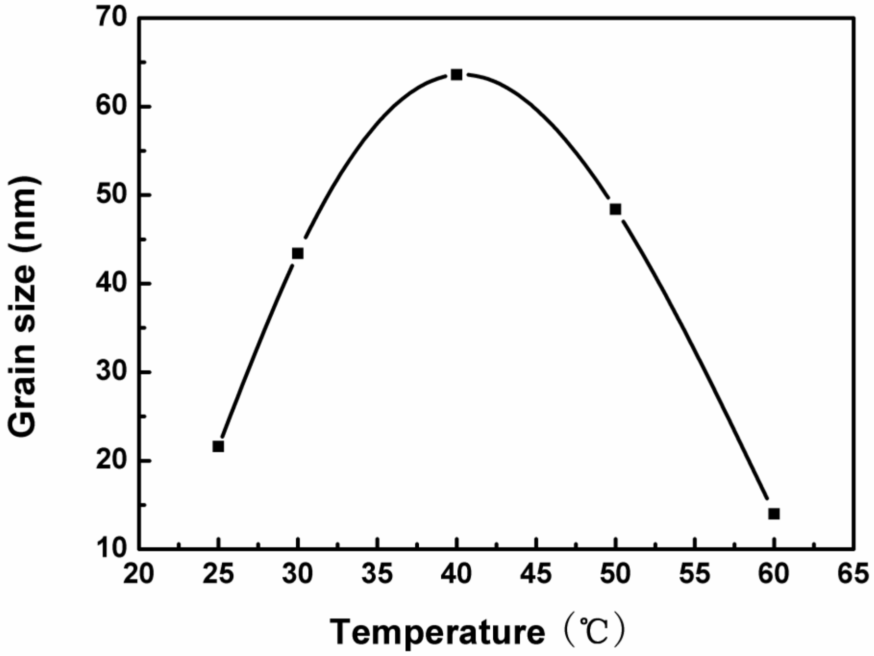

Figure 3. Averaged grain sizes of bcc phase and α-Mn phase in FeCo films electrodeposited at different temperatures

By using Scherrer equation, the averaged grain sizes of bcc phase and α-Mn phase in FeCo films electrodeposited at different temperatures are calculated and shown in Fig.3. It can be seen that with increasing depositing temperature, the averaged grain sizes of bcc phase increase from 21.6 nm (RT) to 63.6 nm (40 ^{o}C). The increased grain size is mainly caused by the high growth rate of grains at high depositing temperature (With increasing electrodepositing temperature, the Fe and Co atoms get more energy which leads to higher diffusion rate and the high diffusion rate results in high growth rate of grains). Further increasing the depositing temperature, the bcc phase transforms to α-Mn phase and the corresponding averaged grain sizes of α-Mn phase decrease from 47 nm (50 ^{o}C) to 14 nm (60 ^{o}C). It can be observed that the films with two phases have a finer grain size than that of the films with single phase, even at higher plating temperatures where diffusion effects usually result in large grain sizes. This is probably caused by the competitive growth of grains in the mixed phase.

4. CONCLUSIONS

FeCo films were electrodeposited on Copper substrates at different temperatures. The composition of Fe-Co films is greatly affected by the electrolyte temperatures. At low temperature (less than 40 ^{o}C) Fe is preferentially deposited due to an inhibiting effect of Fe on the nucleation and growth of Co on the cathode surface. With increasing temperature, the Co content is increased while Fe content is decreased. The crystallographic structure of FeCo films changes significantly with different electrodeposition temperatures. The film grown at RT has a mixed phase (fcc + bcc), but the films deposited at 30 ^{o}C and 40 ^{o}C show only bcc phase. When the electrodeposition temperature is increased to 50 ℃, a metastable α-Mn phase becomes dominant and bcc phase is relatively less in the Fe Co film. Further increasing the temperature to 60 ^{o}C, the film has a mixed phase of α-Mn phase and hcp Co phase. According to the results, elevated electrodeposition temperature promotes the formation of metastable α-Mn phase while the fcc solid solution forms at low temperature. The bcc α-Co_7Fe_3 phase is favored at intermediated temperature. FeCo films with mixed phases have a finer grain size than that of the films with single phase due to the competitive growth of grains in the mixed phase.

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