

Effect of Cobalt Concentration on Structural and Magnetic Properties of Co-Fe Thin Films

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Abstract

Co-Fe films were electrodeposited on Cu substrate from electrolytes with different Co concentration levels. X-ray diffraction (XRD) was used to investigate the films crystal structures. The results indicate that if the Co concentration is less than the Fe concentration, the cubic structure appears in the films, while the hexagonal structure dominates when the Co concentration is sufficiently more than the Fe concentration. The films composition was studied using energy dispersive X-ray spectroscopy (EDX). The EDX results indicate that increasing of the electrolyte Co concentration leads to an increase in the Co content in the Co-Fe alloy films but in a non-linear manner. Morphological observations by scanning electron microscopy (SEM) indicated that the Co-Fe grain size increases when the electrolyte Co concentration is increased. Magnetic measurements by vibration sample magnetometer (VSM) show that the films have in-plane magnetization easy axes. Furthermore, the saturation magnetization increases as the Co concentration increases.

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1. Introduction

Thin films are most commonly prepared by vacuum base techniques such as evaporation, sputtering and molecular beam epitaxy (MBE). In these techniques a material (metal, alloy or semiconductor) is evaporated or sputtered and deposited on a substrate to form a thin film.

Electrodeposition as an alternative deposition technique is economically important because of its low cost and flexibility. It is an inexpensive and versatile method of preparing thin metal films that, unlike most alternatives, does not require a vacuum system.

Despite the simplicity in experimental set up and low cost, the phenomenon of electrodeposition is very complex, since it is typically a non-equilibrium growth process and it involves so many variables such as electrolyte pH and concentration, cation diffusion, and type of substrate. Although electrodeposition of thin films first found widespread applications in decorative and protective coatings, it now plays an important role in producing microelectronic devices in the electronics industry [1].

Electrodeposition usually refers to deposition of a metal or an alloy from an electrolyte by passing a charge between the two electrodes located in the electrolyte. If an external power supply drives a current through the cell, metal ions are reduced to metal atoms at one of the electrodes known as the cathode. The cathode forms the substrate of the electrodeposited film, and is also referred as the working (WE) electrode. To complete the circuit, an oxidation reaction takes place at the second electrode, known as the anode or secondary electrode (SE). The deposition rate for a given electrode depends on the cathode potential (or current density), so that the more negative the cathode potential (or current density), the faster the electrochemical reaction and, therefore the higher the deposition rate [2]. A computer-controlled potentiostat applies a potential difference between the working electrode and the reference electrode (RE). Since the RE is at fixed potential relative to the solution, any change in the potential applied to the working electrode changes the WE potential relative to the solution by the same amount.

Electrodeposition can only take place when there is a conducting path to the external circuit, hence just metallic or semiconductor materials can be used as substrates. This can also be considered as an advantage of electrodeposition to be a

selective method: when a conducting substrate is covered by a patterned resist layer, deposition occurs only where the substrate is exposed. This is particularly important for high-aspect ratio features, because deposition on the resist, which is unavoidable (e.g. in the case of metal evaporation) can easily block them.

Magnetic films have attracted much attention to their potential applications in computer read/write heads. Single ferromagnetic films of transition metals such as Ni, Fe, Co and their alloys exhibit anisotropic magnetoresistance (AMR) [3]. For technical reasons most current applications of magnetic thin films [4], sensor for disk drivers and magnetic random access memory [5], involve the deposition of thin films with crystal texture. Co-Fe alloy coating have been widely used as recording head materials in computer hard drive industries [6], or as a kind of typical magnetic layers for micro electrical mechanical system [7].

In this work we prepared Co-Fe alloy films on (100)-textured polycrystalline Cu substrates. One approach in developing materials with new physical properties is to artificially structure the homogenous alloys.

In order to investigate the effect of the Co concentration on the structural and magnetic properties of Co-Fe alloy films three series of Co-Fe films were deposited from the electrolytes with Co concentrations of 0.01, 0.05 and 0.1 M respectively. The Fe electrolyte concentration was kept constant at 0.01 M in all three electrolytes.

The structural characterization was carried out using XRD patterns, EDX and SEM images, while the magnetic properties were studied by VSM.

2. Experimental procedure

Co-Fe films were grown from an electrolyte containing Co^{2+} and Fe^{2+} ions under the

potentiostatic conditions [8]. The electrolytes were composed of 0.01 M iron sulphate, 0.4 M boric acid and 0.01, 0.05, 0.1 M cobalt sulphate. All materials were dissolved in deionized water. The films deposited in potentiostat mode. A platinum sheet was used as counter electrode. The reference electrode was a saturated calomel electrode. Copper sheet was served as substrate. Prior to deposition, the substrate first was electrodeposited in 50% H₃PO₄ solution with Cu sheet as anode and graphite as cathode. Then copper sheet was washed in 25% H₃PO₄, 10% H₃PO₄ and distilled water respectively. Co-Fe alloy was deposited at room temperature and a cathode potential -1.45, -1.15 and -1 for 0.01, 0.05 and 0.1 M Co concentration, respectively. The electrolyte pH was kept constant at 1.5.

The charge amount required for the film thickness was calculated in according to the Faraday law by assuming 100% current efficiency and the nominal thickness of all films was fixed at 2000 nm. However, the true value of current efficiency is less than 100% due to the hydrogen evolution at the cathode. Thus the film thicknesses reported in this work are nominal film thickness which is less than the real film thickness.

3. Results and discussion

XRD analyses were performed to determine the crystalline structure and phase formation in the Co-Fe deposits. The crystal structure of Co-Fe films deposited at 0.01 M Fe and 0.01, 0.05 and 0.1 M Co concentrations were analyzed and the XRD patterns were given in figures 1(a to c), respectively. As seen from Fig. 1a, reflections from characterize (002), (101) and (106) crystal planes of the hexagonal structure were seen at approximately $2\theta = 45^\circ$, 48° and 89.7° , respectively. In figure 1b, we observe that the (200) peak of the

face-centred cubic (fcc) structure was observed at 51.2° . This peak was observed in 0.05 M Co concentration and was not observed in 0.01 M. Also intensity of (002) peak decreases. In figure 1c, the intensity of (200) peak of fcc structure increases and the intensity of (002) peak of hexagonal structure decreases.

The patterns indicate that the films grown at 0.01 M Co concentration have hexagonal structure and with increase Co concentration in electrolyte, cubic structure appears and dominates to hexagonal structure.

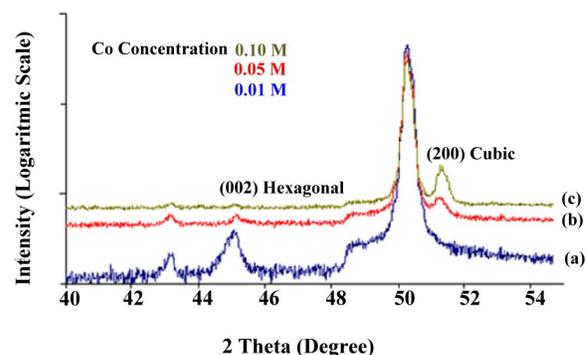


Fig. 1. XRD patterns of Co-Fe films grown the electrolytes with Co concentration of 0.01, 0.05, and 0.1 M.

The EDX results indicate that the film Co content varies as a function of the electrolyte Co concentration but not in a linear manor. The higher electrolyte Co concentration, the more Co content in the Co-Fe films. The results are presented in table 1.

In the situation which the concentrations of Co and Fe are equal, the Co content in the Co-Fe films is more than Fe content. However, when Co concentration is increased by a factor of 5 or 10 (from 0.01 to 0.05 or 0.1 M), the Co content increases but not with the same factors. This result indicate of the existence of anomalous codeposition during the electrodeposition process

and it is in agreement of which is obtained by Qiang et al [9].

Table 1. Compositional measurements of Co-Fe films.

Element	Element concentration in electrolyte	Wt%	At%
Co	0.01	69.47	68.31
Fe	0.01	30.53	31.69
Co	0.05	79.97	79.09
Fe	0.01	20.03	20.91
Co	0.1	91.64	91.22
Fe	0.01	8.36	8.78

Figures 2(a-c) show the SEM images of the films deposited at 0.01, 0.05 and 0.1 M Co, respectively.

As can be seen from the figure, when the electrolyte Co concentration increases, the grain sizes of the Co-Fe films increase, so that, the films which are prepared from the high electrolyte Co concentration (e.g. 0.1 M) contain larger grains compare which are deposited from the electrolyte with low Co concentration (0.01 M). This result may be explained by the phase transition of the deposited metallic atoms. Therefore, the surface morphologies of the films are influenced by the combined action of composition and phase structure.

The average crystalline size for all the Co-Fe films estimated from the diffraction peak widths and using Scherrer equation [10] and the values of 121, 254 and 372 nm are obtained for the films grown from the electrolytes with Co concentrations of 0.01, 0.05 and 0.1 M, respectively. The results support the SEM observations.

Magnetic measurements were performed at room temperature using a VSM instrument and applying magnetic fields in both configurations of parallel and

perpendicular to the film surface The obtained hysteresis loops are shown in figure 3(a-c) for the Fe-Co films grown from the electrolytes with the Co concentration of 0.01, 0.05 and 0.1 M respectively.

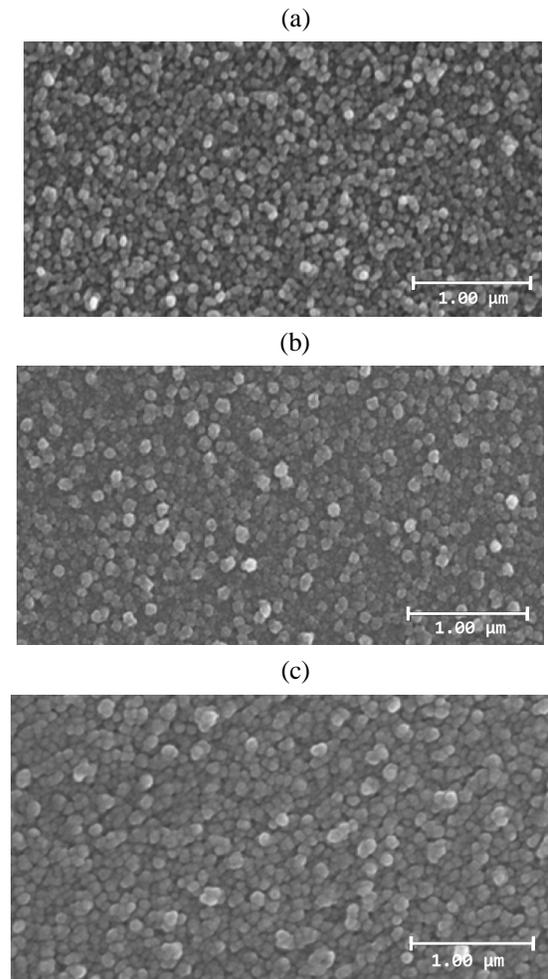


Fig. 2. SEM images of Co-Fe films deposited from the electrolytes with Co concentration of (a) 0.01, (b) 0.05, and (c) 0.1 M.

The in-plane hysteresis loops have a higher remanent magnetization and a lower coercivity compare with the hysteresis loops obtained in perpendicular configuration, indicating that the magnetization easy-axis direction is parallel to the film plane. The coercive field, saturation magnetization and remanence of the samples are summarized in table 2 and 3 respectively.

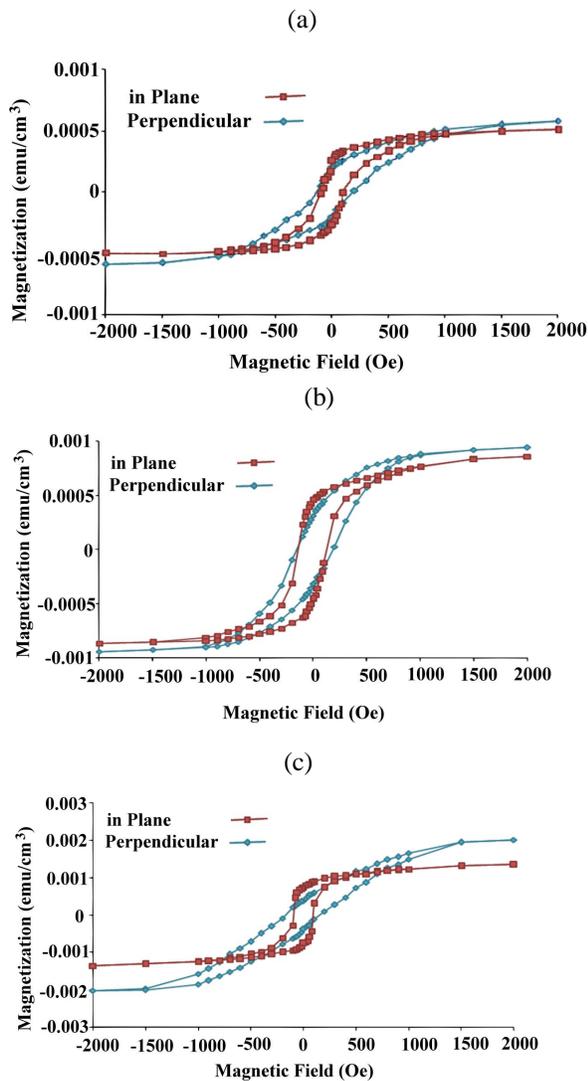


Fig. 3. In-plane and perpendicular hysteresis loops of Co-Fe films deposited from the electrolytes with Co concentration of (a) 0.01, (b) 0.05, and (c) 0.1 M.

Variation of saturation magnetization and remanence of the Co-Fe films (in both in-plane and perpendicular configurations) as a function of the electrolyte Co concentrations are shown in figure 4 and 5 respectively. The coercive field values remain practically unchanged, whereas the saturation magnetization and remanence significantly increases when more Co is increased

in the deposits. These results are in agreement with which is found by Zarpellon and et. al [11].

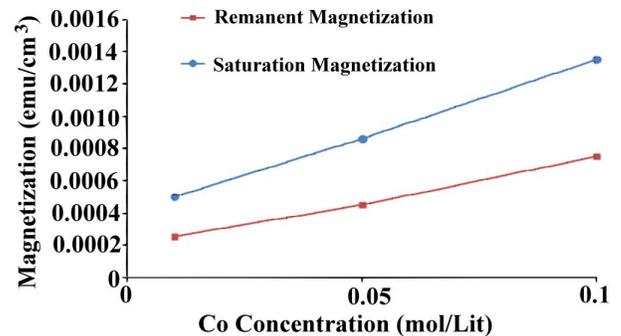


Fig. 4. Influence of Co concentration on remanent and saturation magnetization of Co-Fe alloy films for in-plane configuration.

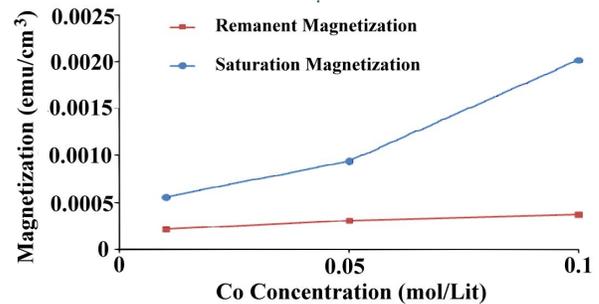


Fig. 5. Influence of Co concentration on remanent and saturation magnetization of Co-Fe alloy films for perpendicular configuration.

4. Conclusion

Co-Fe films were electrodeposited on Cu substrate from the electrolytes with different Co concentration levels. XRD patterns indicate that the structure of the samples significantly depends on the electrolyte Co concentration. The films grown from the electrolyte with Co concentration of 0.01 M have hexagonal structure and by increasing the electrolyte Co concentration, cubic structure appears and dominates the hexagonal structure. Based on the compositional analysis, when the electrolyte Co concentration increases, the film Co content increases but not in the linear manor.

Table 2. Saturation magnetization, coercivity and remanent magnetization of the Co-Fe films grown at different electrolyte Co concentration for in-plane configuration.

Samp	(Co molar, Fe mola)	Saturation magnetizati (emu/cm ³)	Coercivi (Oe)	Remanent magnetizatio (emu/cm ³)
1	(0.01, 0.01)	5.05×10 ⁻⁴	98.2	2.58×10 ⁻⁴
2	(0.01, 0.05)	8.60×10 ⁻⁴	146	4.52×10 ⁻⁴
3	(0.01, 0.1)	13.50×10 ⁻⁴	96.65	7.51×10 ⁻⁴

Table 3. Saturation magnetization, coercivity and remanent magnetization of the Co-Fe films grown at different electrolyte Co concentration for perpendicular configuration.

Sample	(Co molar, Fe molar)	Saturation magnetization (emu/cm ³)	Coercivity (Oe)	Remanent magnetization (emu/cm ³)
1	(0.01, 0.01)	5.58×10 ⁻⁴	180.9	2.15×10 ⁻⁴
2	(0.01, 0.05)	9.40×10 ⁻⁴	187.65	3.12×10 ⁻⁴
3	(0.01, 0.1)	20.15×10 ⁻⁴	178	3.77×10 ⁻⁴

This result supports the existence of anomalous codeposition during the electrodeposition process. The morphological investigation indicates that Co-Fe alloy grain sizes increase, when the electrolyte Co concentration increases. Magnetic measurements reveal that all of the films have an in-plane easy axis direction. While the remanent and saturation magnetization increase as the electrolyte Co concentration increase, the coercive field remains almost unchanged.

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