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Characterisations of CoCu films electrodeposited at different cathode potentials

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ABSTRACT

Structural and magnetic properties of CoCu films electrodeposited on polycrystalline Cu substrates were investigated as a function of cathode potential used for their deposition. The compositional analysis, performed by energy dispersive X-ray spectroscopy, demonstrated that an increase in the deposition potential results in an increase in Co content of CoCu films. The crystal structure of the films was studied using the X-ray diffraction (XRD) technique. It was observed that they have a face centred cubic (fcc) structure, but also contain partly hexagonal close-packed phase. XRD results revealed that the (1 1 1) peak of fcc structure splits into two as Co (1 1 1) and Cu (1 1 1) peaks and the peak intensities change depending on the deposition potential and hence the film composition. The magnetic measurements were carried out at room temperature using a vibrating sample magnetometer. The magnetic findings indicated that coercivity decreases and saturation magnetisation increases with the increase of Co:Cu ratio caused by the deposition potential and also all films have planar magnetisation.

1. Introduction

Ferromagnetic films consisting of transition metals (e.g. Fe, Ni, Co) or their alloys have a wide range of applications in data storage devices, write–read heads, and sensor technology. Especially Co-based magnetic films are used in microelectromechanical systems (MEMSs), including microactuators, sensors, micromotors, etc. [1–4]. Production of ferromagnetic films using several deposition techniques has aroused great interest because many of their properties change with preparation methods as well as deposition parameters [5,6]. Electrodeposition has been one of the techniques used to produce ferromagnetic single, alloy, and multilayer films for a long time, since it has some advantages such as low cost, simplicity and fast production. The structural and magnetic properties of electrodeposited films are highly affected by deposition parameters [7]. One of the most effective parameters is the deposition potential, which affects film composition and microstructure, and hence magnetic properties [8–11].

In this study, the role of cathode potential on crystal structure and magnetic properties of CoCu films electrodeposited on polycrystalline Cu substrates was studied. It was found that the CoCu film properties change significantly with the cathode potential used to deposit them.

2. Experimental

The electrodeposition was carried out in a three-electrode cell using EGG-362 model potentiostat/galvanostat. The anode was a platinum (Pt) sheet. Saturated calomel electrode (SCE) served as a reference electrode and (1 1 0) textured polycrystalline Cu substrates were used as the cathode. Prior to electrodeposition, Cu substrates were electrochemically polished in a 50 vol% phosphoric acid solution. CoCu films were deposited potentiostatically from an electrolyte containing 0.5 M $CoSO_4 \cdot 7H_2O$, 0.05 M $CuSO_4 \cdot 5H_2O$, and 0.3 M H_3BO_3 at room temperature. The films were deposited at the cathode potentials of -1.6, -1.5, -1.4, -1.3, -1.2, -1.1, and -1.0 V vs. SCE. The electrolyte pH was 2.5. The film thickness was fixed at 5 μm.

The crystal structure of the films was studied using X-ray diffraction (XRD-Rigaku rint 2200). XRD patterns were obtained using CuK_α radiation (λ=1.54056 Å) in the range 2θ=40°–100° with a step size 0.02°. The film composition and surface morphology were determined with an energy dispersive X-ray spectroscopy (EDX) and a scanning electron microscope (SEM-Zeiss Supra 50Vp), respectively. The magnetic measurements were performed using a vibrating sample magnetometer

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(VSM-ADE EV9 model) in the field range of ± 20 kOe at room temperature.

3. Results and discussion

In the first step of this investigation, the electrolyte was characterised by cyclic voltammetry (CV) to find appropriate cathode potentials for the deposition of CoCu films. The scan was started in the cathodic direction from +1.0 to −1.8 V and the potential scanning rate was 20 mV/s. The stabilized CV curve (second or further cycles) obtained from an electrolyte containing Cu only is given in Fig. 1. As seen in Fig. 1, a Cu deposition peak appears at around −0.5 V and this is followed by a low current flow. As the potential increases after −1.4 V, the current slightly begins to increase. When the scan was reversed, an anodic peak was seen at around +0.4 V, corresponding to Cu dissolution. The CV curve of the electrolyte used to deposit CoCu films is given in Fig. 2. A low current on the cathodic side at around −0.4 V corresponds to reduction of Cu^{2+} ions. In the potential range between −0.4 and −1.0 V, a current plateau with low current occurs, indicating diffusion limited deposition of Cu. Beyond −1.0 V, the cathodic current begins to increase and rises continuously due to the deposition of Co and possibly also because of H_2 generation. In the reversal of the scan direction, the current decreases with decreasing potential and then an anodic current begins to flow at about −0.6 V. A broad anodic peak appears between −0.6 and +0.4 V, due to combination of the peaks corresponding to the dissolution of Co and Cu. Based on potentiodynamic measurements and appearance of proper films, the deposition potential range of CoCu films was decided to be between −1.0 and −1.6 V. Current–time transients were also recorded during the deposition process in order to control the stability of deposition. The transients for films grown at different deposition potentials are given in Fig. 3. It is clearly seen that the films were deposited correctly and orderly since the current values are stable for each deposition potential.

In order to differentiate reflections from the Cu substrate and CoCu films, firstly XRD measurements of the Cu substrate were analysed and their XRD patterns were observed to have reflections from only (2 0 0), (2 2 0), and (3 1 1) planes of face centred cubic (fcc) structure. The XRD patterns also showed that Cu substrates have a strong (1 1 0) texture. The XRD patterns of CoCu films grown at −1.0, −1.3, and −1.6 V are given in Fig. 4. The XRD measurements of the films were made on their Cu substrates. Note that the films also give (2 0 0), (2 2 0), and (3 1 1) reflections of fcc structure, which almost coincide with those of Cu substrates. In addition to these reflections, the films also contain the (10.0) peak of hexagonal close-packed (hcp) apart from fcc at $2\theta \approx 41^\circ$ as seen in Fig. 4. This indicates that CoCu films have a mixed crystal structure consisting of mostly fcc and hcp. Furthermore, the films have two separate peaks at the angular position of $2\theta \approx 44^\circ$. One of them that appeared at low angle corresponds to the (1 1 1) peak of fcc Cu and the other seen at high angle to the (1 1 1) peak of fcc Co. This means that the (1 1 1) planes of Co and Cu develop independently during the growth of the film, since the (1 1 1) peak of Cu substrate did not appear on the XRD pattern. The result indicates that the CoCu system is

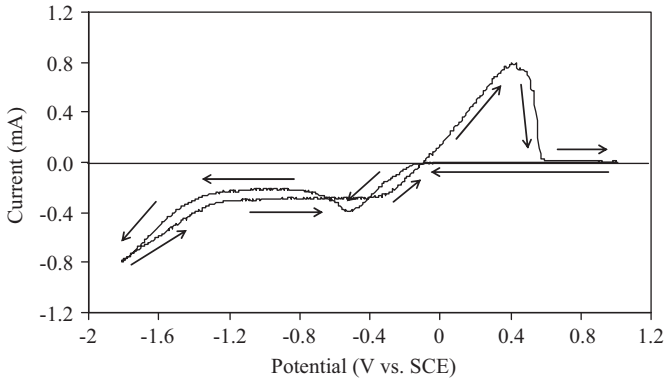

Fig. 1. Cyclic voltammetry curve of the electrolyte containing only Cu (devoid of Co). The arrows show the scan direction.

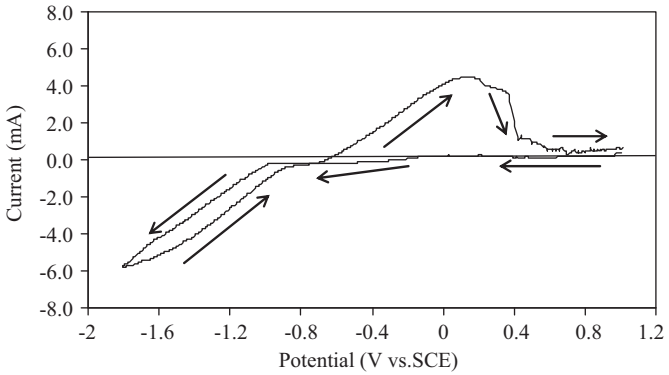

Fig. 2. Cyclic voltammetry curve of the electrolyte used to deposit CoCu films. The arrows show the scan direction.

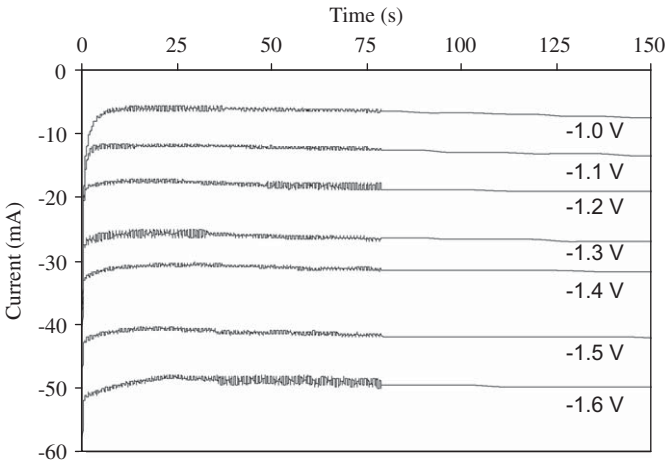

Fig. 3. Current–time transients of CoCu films deposited at different cathode potentials.

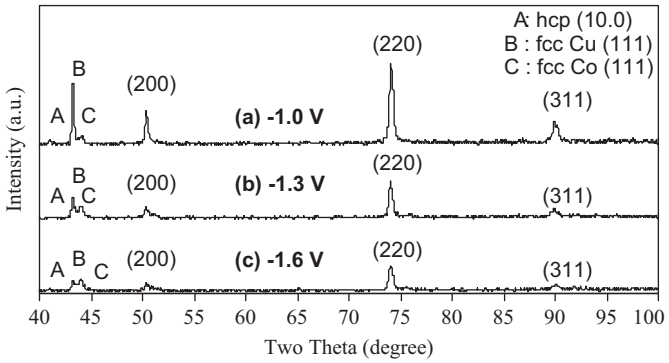

Fig. 4. XRD patterns of CoCu films grown at (a) −1.0, (b) −1.3, and (c) −1.6 V.

Table 1
Compositional analysis and magnetic data of CoCu films.

Cathode potential (V vs. SCE)	Composition analysis (EDX) (wt%)		Magnetic measurements (VSM)	
	Cu	Co	H_c (Oe)	M_s (emu/cm^3)
−1.0	77	23	129.38	174.33
−1.1			96.60	360.50
−1.2			88.31	383.89
−1.3	58	42	66.97	528.09
−1.4			64.42	600.27
−1.5			60.29	633.72
−1.6	50	50	56.69	668.25

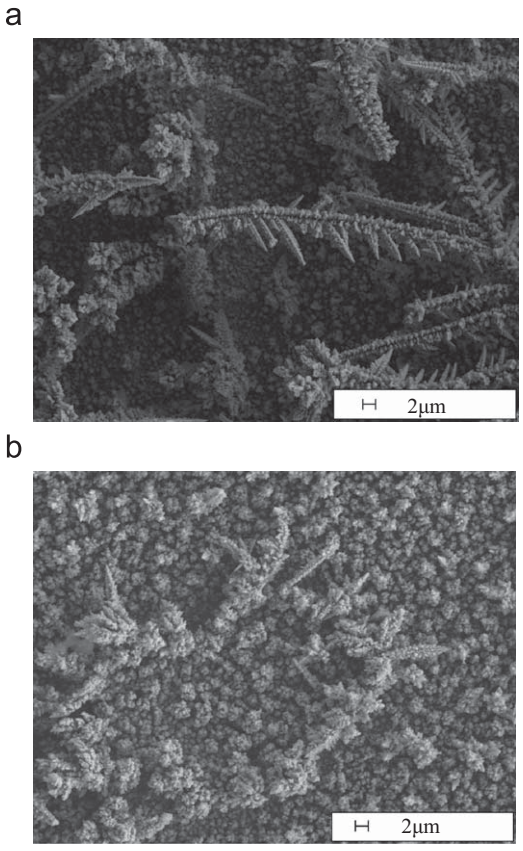

Fig. 5. SEM micrographs of CoCu films grown at (a) low (−1.0 V) and (b) high (−1.6 V) deposition potential.

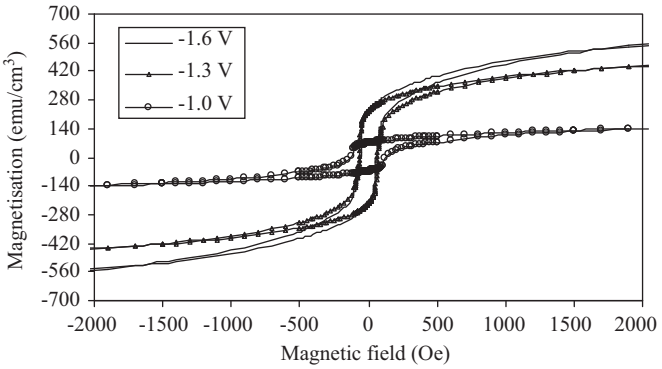

Fig. 6. In-plane hysteresis loops of CoCu films deposited at −1.0, −1.3 and −1.6 V.

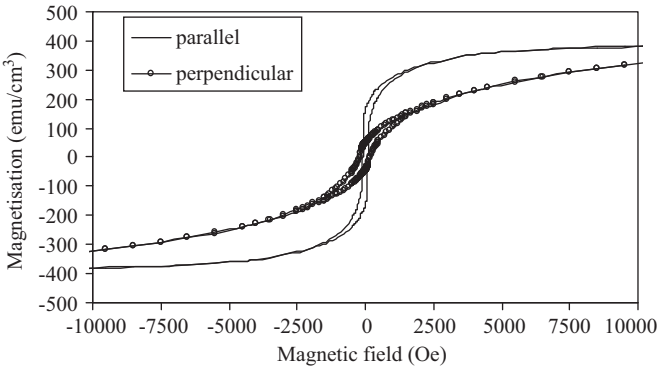

Fig. 7. Parallel and perpendicular hysteresis loops for the film deposited at −1.4 V.

immiscible as is well known [12,13]. The split of the (1 1 1) peak may arise from the (1 1 1) preferred orientation of Cu, because growth of Cu in the (1 1 1) direction is favoured. On the other hand, it is clearly seen that the intensity of the Cu (1 1 1) peak becomes weaker as the deposition potential increases. This change in sequence is also seen for the rest of the films, which are not shown here. This is probably due to an increase of the Co content in the film with increasing deposition potential as seen in EDX data in Table 1. It is well known that Co deposition in an electrolyte containing Co and Cu is dominant at high electrode potentials.

The morphological investigation showed that CoCu films have dendritic structures. As an example, SEM pictures of the films grown at low (−1.0 V) and high (−1.6 V) deposition potentials are shown in Fig. 5. The film deposited at −1.0 V consists of straight backbones with side branches. EDX analysis showed that the branches and sub-branches are Cu-rich while the base of the film is Co-rich. At high potential (−1.6 V), initial stage of the dendritic growth was observed in the films and they look like cauliflower structures. Besides, in some parts there are Cu-rich growing branches. To the EDX results, the reason of dendritic formation is high Cu content in the film. As Cu content decreases from 77 to 50 wt% (see Table 1), the length of branches shortens and less dense dendritic structures form. Therefore, the density of branched structure may be attributed to the composition of the film that was affected by deposition potential.

Magnetic measurements were performed in magnetic fields applied in the film plane and perpendicular to the film plane at room temperature. Fig. 6 shows in-plane hysteresis loops of CoCu films deposited at −1.0, −1.3, and −1.6 V. It can be clearly seen that it is harder to magnetise the films grown at lower deposition potentials, on account of having more Cu content in the films. The

results obtained from VSM are listed in Table 1. As the deposition potential increases, coercivity, H_c decreases, while the saturation magnetisation, M_s increases. This effect can be attributed to the change of Co:Cu ratio in the film caused by the change of deposition potential. As mentioned in the structural analysis, CoCu system is not a solid solution. Therefore, its magnetic properties can be related only to Co. The M_s values found in this study are lower than that of bulk Co (1420 emu/cm^3). However, M_s of the films increases as the Co content increases. The perpendicular hysteresis loops have lower remanent magnetisation and higher coercivity than the in-plane loops for all films. This indicates that easy-axis direction of the magnetisation is parallel and hard-axis is perpendicular to the film plane. As an example, parallel and perpendicular hysteresis loops for the film grown at -1.4 V are shown in Fig. 7.

4. Conclusions

It was observed that the crystal structure of CoCu films produced by electrodeposition changed with Co:Cu ratio, which was affected by the cathode potential used to deposit them. CoCu films had mostly fcc and partly hcp mixed phase. The (1 1 1) peak of fcc structure splits into two as Co (1 1 1) and Cu (1 1 1). Intensities of the fcc (1 1 1) peaks change with composition of the film caused by changes in deposition potential. Surface morphology of the films indicates dendritic growth when they are grown at a low potential (-1.0 V), while they have mostly roundish cauliflower shapes when grown at a high potential (-1.6 V). Also, magnetic properties were obviously influenced by the deposition potential. A decrease of deposition potential results in an increase of the Cu content in the film; hence a rise in coercivity and a reduction in saturation magnetisation occur. Furthermore it is seen that easy-axis direction of the magnetisation is parallel to the film plane. The results are useful for possible production of CoCu films with a range of magnetic properties for applications when considering sensors and recording media.

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