Electrochemical preparation and magnetic properties of Co–Cu nanometric granular alloy films

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Abstract. A detailed electrodeposition of Co–Cu nanometric granular alloy films in citrate solution has been performed based on a galvanostatic technique. Electrochemical behaviour of the bath solution containing both Co^{2+} and Cu^{2+} was investigated by linear sweep voltammetry. Cathodic polarization curves indicated that high quality Co–Cu nanometric granular alloy films can be obtained at room temperature with a pH of 6 and current density equal to or more negative than -1.0 mA cm^{-2} . Magnetic properties of the films were measured at room temperature by the physical property measurement system. Magnetization curves of the as-prepared Co–Cu nanometric granular alloy films displayed superparamagnetism (SPM). However, after annealing at 450°C for 1 h, magnetic property of the films changed from SPM to ferromagnetism. Meanwhile, the annealed Co–Cu nanometric granular alloy films showed an increase in saturation magnetization with the increase of the current density.

Keywords. Electrodeposition; granular film; Co–Cu alloy; magnetic property.

1. Introduction

Co–Cu multilayer or granular films are of great interest due to their high resistivity [1], magnetism and magneto-transport [2–6]. These excellent properties have brought interesting potential applications for magnetic read heads and sensors. Generally, Co–Cu granular films could be obtained by the application of various techniques, such as magnetron sputtering, molecular beam epitaxy, ion-beam sputtering and electrodeposition [7–16]. Among them, electrodeposition has been regarded as a successful one to produce films with practical technological applications due to its advantages of cost effectiveness, ease of processability, large area deposition and relatively low temperature [17].

To date, many studies on Co–Cu granular films have been focused on properties or structure [1,18–21] with little consideration of the procedure for the preparation of good quality films. In order to obtain film with good quality by electrodeposition methods, it is necessary to determine the electrochemical behaviour of electrolytes as a function of electrolyte composition, pH value and temperature. Herein, a detailed report of the preparation of Co–Cu nanometric granular alloy films in citrate bath by galvanostatic deposition is presented. Electrochemical behaviour of a trisodium citrate solution containing both Cu^{2+} and Co^{2+} was initially investigated by linear sweep voltammetry. And then the Co–Cu

nanometric granular alloy films were formed on indium-tin oxide (ITO) coated glass substrates by galvanostatic deposition at room temperature with a pH of 6. In addition, magnetic properties of the Co–Cu nanometric granular alloy films are discussed in detail.

2. Experimental

2.1 Solution preparation

Co–Cu nanometric granular alloy films were deposited from an electrolyte solution containing $0.27 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O}$, $0.12 \text{ M CoSO}_4 \cdot 7\text{H}_2\text{O}$, $2.3 \text{ M Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 0.57 M NaCl , which was prepared from analytical-grade reagents and redistilled water. The electrolyte pH was adjusted by adding sodium hydroxide or sulphuric acid solution with a concentration of 0.1 M . The solution was sparged with nitrogen for 45 min to remove any dissolved oxygen before the electrodeposition experiment.

2.2 Polarization measurement

Polarization measurements were performed in a glass cell containing an ITO coated glass electrode with a working area of $10 \text{ mm} \times 20 \text{ mm}$, a graphite cylinder counter electrode,

and a saturated calomel reference electrode. Voltammograms were recorded using an LK2005A electrochemical workstation controlled with a computer. Before each experiment, the ITO electrodes were successively cleaned with acetone, ethanol and ultrasonically in redistilled water. The solutions were not stirred during measurements. The linear voltammogram measurements were started at open circuit potentials with the scan rate of 20 mV s^{-1} . The end potential and equilibration time were set to -1.6 V and 10 s , respectively.

2.3 Electrodeposition experiments

Preparation of Co–Cu granular alloy films in citrate bath was performed on ITO coated glass substrates by galvanostatic deposition. The deposition experiments were carried out in a bath solution with a pH of 6 at room temperature. Current densities between -0.8 and -1.2 mA cm^{-2} were typically employed and the duration of each experiment was 30 min . Other conditions were the same as those in the above polarization measurements. As a result, Co–Cu granular alloy films with thickness between 50 and 100 nm were obtained. On completion of an experiment, the cathode was removed from the solution, rinsed in redistilled water, and then dried under a stream of nitrogen gas. The subsequent thermal annealing of the films was carried out in a vacuum furnace at 450°C for 1 h at a heating rate of 5°C min^{-1} and then brought to room temperature.

2.4 Microstructural and magnetic examination

Morphology of the Co–Cu nanometric granular alloy films was studied using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800). The crystallographic structure was examined using an X-ray diffractometer (XRD) with Cu $K\alpha$ radiation. The compositions were analysed by energy dispersive spectrometry (EDS). Magnetic measurements were carried out using a physical property measurement system (PPMS-6700) at room temperature.

3. Results and discussion

3.1 Polarization measurement

3.1a Electrochemical behaviour of electrolytes: The quality of the surface of films prepared by galvanostatic deposition was strongly dependent on the applied current density during electrodeposition. To obtain good quality films, electrochemical behaviour of the electrolyte should be first investigated. Polarization experiments were therefore carried out at room temperature, in solution with a pH of 6, containing Co^{2+} , Cu^{2+} and both Co^{2+} and Cu^{2+} . The corresponding polarization curves are plotted in figure 1. The polarization data obtained from the copper-free (curve 1) and cobalt-free (curve 2) citrate solutions indicate that the deposition of copper and cobalt species commence at about -0.45 and -1.0 V , respectively. Noted that the current plateau observed in curve 3 at

Figure 1. Cathodic scanning process in bath solution with different cations at room temperature and with a pH of 6, the scan rate is 20 mV s^{-1} .

potentials between -0.45 and -1.0 V corresponds to the deposition of copper species according to curve 2. At potentials of around -1.0 V , there is a rapid increase in the measured current due to the commencement of cobalt deposition. In the potential range of -0.45 to -1.0 V , the occurrence of the copper deposition under diffusion control may be responsible for the current plateau. In addition, the data of curve 3 indicates that at more negative potentials than -1.0 V the co-deposition of copper and cobalt species may occur.

3.1b Effect of temperature and pH on electrolyte polarization: In order to assess any differences in the electrochemical behaviour of the electrolytes with different pH values, polarization experiments were performed in solution containing both Co^{2+} and Cu^{2+} ions. The polarization curves are plotted in figure 2a. The polarization data indicate that a current plateau was observable in each curve. The plateau becomes short and obviously shifts to the right as the pH value decreases, which can be attributed to the hydrogen evolution reaction. Figure 2b shows the differences in the electrochemical behaviour of the electrolyte with a pH of 6 at different temperatures. No obvious current plateau is observed at high temperature, which can be mainly attributed to aggravation of copper and cobalt diffusion with the increase of temperature. The results of figures 1 and 2 imply that room temperature and pH of 6 are more favourable for electrodeposition of Co–Cu films. At potential around -1.0 V , good quality Co–Cu nanometric granular films can be obtained. The current density corresponding to the potential is in the range from -0.8 to -1.2 mA cm^{-2} (see curve 1 in figure 2b).

3.2 Electrodeposition experiments

3.2a Structural and composition analysis: Structures of the Co–Cu films were studied using an XRD in the 2θ range

Figure 2. Cathodic polarization curves of bath solutions with both Co^{2+} and Cu^{2+} ions at different conditions, the scan rate is 20 mV s^{-1} : (a) different pH values at room temperature and (b) different temperatures at pH 6.

from 40 to 50°. The results indicate that all the as-prepared films show the same face-centred cubic (fcc) Cu structure (shown in figure 3a). An intense (111) peak is observed at the positions of the corresponding Bragg reflections of the fcc phase of Cu metal. Note that no diffraction peak of Co is detected. However, for the samples prepared with the applied current density equal to or more negative than -1.0 mA cm^{-2} and annealed at 450°C for 1 h, a relatively small peak of Co (111) with fcc structure appears at the right shoulder of the Cu (111) peak (see figure 3b).

To clear the above phenomenon, EDS analysis was performed. The results indicated that except for the film prepared with the applied current density more positive than -1.0 mA cm^{-2} , all the films consisted of both Cu and Co elements. Compositions of the films prepared at all conditions are listed in table 1. From the table, we can conclude that the Co content increases with an increase of the applied current density. It is in good agreement with figure 1. The results implied that except for the films prepared at current density more positive than -1.0 mA cm^{-2} , a metastable alloy phase of the Co–Cu is formed at room temperature in the as-deposited condition. The X-ray diffraction is not sensitive to a relatively low concentration of Co-rich phase with extremely fine Co particle at its core or in the form of cluster, which is responsible for the absence of Co peaks in the as-deposited films. After annealing at 450°C for 1 h, a very weak peak (111) of Co-rich phase was observed in the XRD due to the growth of Co grains *via* diffusion.

3.2b Morphology characterization: The Co–Cu electrodeposits obtained in all conditions had a smooth coppery appearance. This similarity in surface appearance was also evident in EDS of the Co–Cu electrodeposits with a small amount of Co content. Surface morphology was further characterized by FE-SEM. The results demonstrated that Co–Cu nanometric granule alloy films were prepared under conditions of current density equal to or more negative than

-1.0 mA cm^{-2} , and that the as-prepared films had a similar morphology. The typical SEM images are shown in figure 4. It clearly shows that the surface of the film consisted of compact and nodular structures about 500 nm (see figure 4a). Moreover, each nodular structure contained second phase Co particles which are the bright white spots in figure 4. Some typical Co particles in figure 4 were marked using a yellow dot circle curve. As shown in figure 4a, the size of Co particles is less than 20 nm. They appear like islands did not dispersed embedded in a Cu matrix with nodular structures. It is proved that Co–Cu nanometric granule alloy films were successfully prepared under our experimental conditions.

The size of Co particles became larger than 20 nm after the film was annealed at 450°C for 1 h (see figure 4b). It indicated that the separation of Co phase from Cu phase took place during annealing which is in agreement with XRD patterns (shown in figure 3b). It is well known that Co and Cu elements are nearly immiscible, and no equilibrium phases exist in the Co–Cu binary phase diagrams [22]. However, the high electrodeposition rate during sample preparation may result in a metastable Co–Cu alloy film with extended solubility. Spinodal decomposition may occur in the films during electrodeposition, which leads to the nucleation of Co grains dispersed and embedded in the Cu matrix. In the process of annealing, the extremely fine Co particle at its core or in the form of cluster was dissolved again and aggregated into bigger Co particles which increased the size of the Co cluster.

3.3 Magnetic measurement

The magnetization curves of the samples were measured at room temperature with decreasing magnetic field after saturation in $H = 10 \text{ kOe}$. To eliminate influence of ITO coated glass substrates used in our experiment, magnetic property of the substrates was initially measured by PPMS-6700.

Figure 3. XRD patterns of Co–Cu nanometric granular films with different applied current density and a pH of 6: (a) the as-prepared at room temperature and (b) after thermal annealing at 450°C for 1 h.

Table 1. Results of chemical composition analysis of Co–Cu nanometric granular alloy films prepared with different applied current density.

Current density (mA cm ⁻²)	Cobalt content (at%)	Copper content (at%)
–0.8	—	100
–0.9	—	100
–1.0	1.7	98.3
–1.1	1.9	98.1
–1.2	2.3	97.7

The results demonstrated that the ITO coated glass substrates did not display magnetism. The as-prepared samples with substrates were then measured. A typical result is plotted in figure 5a for the nanometric granule alloy film prepared with applied current density -1.1 mA cm^{-2} . The inset shows the partial hysteresis loop at low magnetic fields from which the coercive field $H_c = 25 \text{ Oe}$ and remanent magnetization $M_r = 110 \text{ emu cm}^{-3}$ can be deduced.

It was observed that technical saturation of the ferromagnetism (FM) contribution was reached at about $H_s = 1.5 \text{ kOe}$. However, figure 5a indicates that there is a strong variation of the magnetization up to the highest magnetic fields applied. The change of high-field magnetization originates from superparamagnetism (SPM) regions in the nanometric granule alloy

film. The magnetization curves for $H > H_s = 1.5 \text{ kOe}$ could be described as

$$M(H) = M_{\text{FM}} + M_{\text{SPM}}L(x) \quad (H > H_s). \quad (1)$$

Here, M_{FM} and M_{SPM} are the room temperature saturation magnetization values for the FM and SPM component, respectively, and $L(x)$ is the Langevin function with $x = \mu H/kT$. The average magnetic moment of a SPM region is given by $\mu = N_M \mu_B$ with μ_B as the Bohr magneton, N_M is the number of SPM particles and the subscript M refers to the fact that N was deduced from magnetization data. The fit of the experimental data in figure 5a with equation (1) for $H >$

Figure 4. SEM images of typical Co–Cu nanometric granule films with applied current density -1.1 mA cm^{-2} : (a) the as-prepared at room temperature and (b) after thermal annealing at 450°C for 1 h.

Figure 5. (a) Room-temperature magnetization data (o) for the as-prepared Co–Cu nanometric granule alloy film with the applied current density -1.1 mA cm^{-2} , the solid line corresponds to the Langevin fit for $H > 1.5 \text{ kOe}$. The inset showing details of the hysteresis loop at low magnetic fields and the value of the coercive field (H_c). (b) Hysteresis loop of the Co–Cu nanometric granule alloy film annealed at 450°C for 1 h.

$H_s = 1.5 \text{ kOe}$ is displayed by the solid line, demonstrating a good SPM behaviour for high magnetic fields. From the fit, the parameters $M_{\text{FM}} = 1.5 \times 10^3 \text{ emu cm}^{-3}$, $M_{\text{SPM}} = 2.55 \times 10^3 \text{ emu cm}^{-3}$, and $N_M = 1832$ are deduced. Very similar results were obtained for films prepared with applied current density -1.0 and -1.2 mA cm^{-2} . The fitting parameters, coercive field and remanent magnetization data are collected in table 2. The results indicate existence of SPM regions in the as-prepared Co–Cu nanometric granule alloy films. In addition, the H_c increased with increasing current density (see table 2). It is in agreement with Co–Ag granular films reported by the Voiron group [23].

The SPM regions with so-called ‘loose moments’ were Co-rich phase formed during electrochemical processes [24]. As described in XRD section, the Co-rich phase is in the form of extremely fine Co particle at its core or in the form of cluster. Therefore, the film can exhibit a SPM

behaviour. A similarly shaped curve has been observed for a superparamagnetic sample [23–25].

However, hysteresis loops of the film annealed at 450°C for 1 h display ferromagnetic behaviour. As shown in figure 5b, the hysteresis loop exhibits a large coercive field splitting ($\gg 100 \text{ Oe}$) and a fast saturation in the field below 2000 Oe , which are much different from the as-prepared sample. This distinct behaviour suggests a change in the magnetic structure of the annealed clusters which grew larger than 20 nm (see figure 4b). The magnetization in the cores of the clusters is non-uniform. Thus possibly domains are built. The magnetization dynamics is different from the mono-domain Langevin behaviour for small particles. During the annealing process, particles coalesce and incorporate isolated Co-single ion spins in a metallic non-monodomain cluster which increases the saturation magnetization to $5.5 \times 10^3 \text{ emu cm}^{-3}$, higher than the nonsaturated value of $3.6 \times 10^3 \text{ emu cm}^{-3}$ in figure 5a.

Table 2. Magnetic parameters (saturation magnetization M , coercive field H_c and remanent magnetization M_r) of the as-prepared Co–Cu nanometric granule alloy films investigated.

Current density (mA cm^{-2})	$M_{\text{FM}} \times 10^3$ (emu cm^{-3})	$M_{\text{SPM}} \times 10^3$ (emu cm^{-3})	N_{M}	H_c (Oe)	M_r (emu cm^{-3})
–1.0	1.5	1.9	1700	12	105
–1.1	1.5	2.55	1832	25	110
–1.2	1.7	3.8	2100	39	86

The saturation magnetization values of the ferromagnetic (M_{FM}) and superparamagnetic (M_{SPM}) components as well as parameter N_{M} were deduced by fitting the experimental data to equation (1).

Figure 6. Out-of-plane hysteresis loop of Co–Cu nanometric granule alloy film with different applied current density, annealing at 450°C for 1 h and measured at room temperature.

The hysteresis loop in figure 5b also displays a slight magnetic anisotropy in directions between the out-of-plane and in-plane. This is different from general film whose direction of easy magnetization is in-plane. However, according to XRD patterns in figure 3b, the Co grains in annealing Co–Cu nanometric granule alloy films grow on the preferred orientation (111) which is perpendicular to the ITO coated glass substrates. The direction of easy magnetization of Co phase with the fcc structure is along the (111) crystallographic plane. As a result, the in-plane hysteresis is flatter than the out-of-plane hysteresis.

Magnetic properties of Co–Cu nanometric granule alloy films synthesized at different current density and annealed at 450°C for 1 h were measured at room temperature. Figure 6 shows that saturation magnetization of the Co–Cu nanometric granule alloy film increases with the increase in the applied current densities, which is due to the increase in the Co content (see table 1).

4. Conclusions

The Co–Cu nanometric granular alloy films were successfully electrodeposited using a galvanostatic technique. The structural and magnetic characterization indicated the formation of

a Co-rich phase with extremely fine Co particles at its core or in the form of cluster in the as-prepared films, which is responsible for the superparamagnetic behaviour. After annealing at 450°C , magnetic property of such films changed from SPM into FM, which is related to the growth of the Co particles. Moreover, on increasing current density, the saturation magnetization of the annealing Co–Cu nanometric granule alloy film increases, which could be attributed to the increase of Co content.

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