Electrodeposition of Cu-Co Multilayer Films

By J. Xue, J. Wu and D. Yang

Cu-Co multilayer film has been produced from a single bath by electrodeposition. The effects of the concentration of copper ions, current density and the speed of rotation were investigated. The results were analyzed by TEM, AES and X-ray diffraction. The results indicated that the film possessed layered structure, consisting of alternating pure copper and copper-cobalt alloy layers. The copper content of the alloy layers increased with increase of concentration of copper ions in solution and with increase of rotation speed.

Multilayer film, consisting of magnetic and non-magnetic layers, is a new research field actually in rapid development in recent years. New magnetic properties are revealed as different from those of bulk materials, such as perpendicular magnetization, large magnetoresistance, etc.[1-3] Moreover, the film has potential applications to high-density magnetic recording and to magnetic sensors.

Studies have been made of the properties of multilayer film prepared by vapor-deposition and sputtering techniques.[2-4] Some authors have also reported the properties of multilayer film prepared by electrodeposition.[5,6] In this study, we show production of Cu-Co multilayer film successfully from a simpler electrolyte.

Experimental Procedure

Equipment

A copper disc, 16.6 mm in diameter, was used as substrate material. It was mounted in a specially designed sample holder that left exposed a 1.5-cm^2 area. The counter-electrode was a 3-cm^2 platinum sheet. The multilayer films were obtained using the dual potential pulse method. The first potential pulse is low, about -550 mV (vs. SCE), to produce copper. The second potential pulse is high, about -1.1 V ~ -1.8 V (vs. SCE), to produce cobalt. The dual potential pulses were generated by pulse generator and controlled by computer.

Electrolyte and Sample Preparation

The electrolyte composition is listed in the table. Prior to deposition, the substrates were polished with abrasive paper, up to No. 1000, then mechanically polished until a bright surface was obtained, followed by degreasing and rinsing.

Cathode Polarization Measurement and Analysis

Cathode polarization was carried out with a horizontal platinum counter-electrode facing the disc, at a scan rate of 1 mV/sec. The reference electrode was a saturated calomel electrode. The crystallographic structures of multilayers were studied using a diffractometer in Cu-Kα radiation. The composition and depth profile of the multilayers were analyzed by SEM, TEM and AES.

Electrolyte Composition

$CuSO_4 \cdot 5H_2O$	0.003-0.01 mol/L
$CoSO_4 \cdot 7H_2O$	0.35 mol/L
Additive	50-70 mL/L
Temp	20-30 °C
pH	5-7

Results and Discussion

Figure 1 shows cathodic polarization curves. From the curves, it is obvious that copper deposition is mass-transfer-controlled over several hundred mV above the potential range for cobalt deposition. It is not difficult to deposit pure copper layer potentiostatically between -300 mV and -650 mV. This is also confirmed by the analytical results. When the potential was switched above -750mV, the cobalt began to be deposited together with the copper. The content of copper in the alloy layer is variable with the conditions of the deposition. At first, it increased with increase of concentration of copper ions in the electrolyte, and controlled as expressed by the

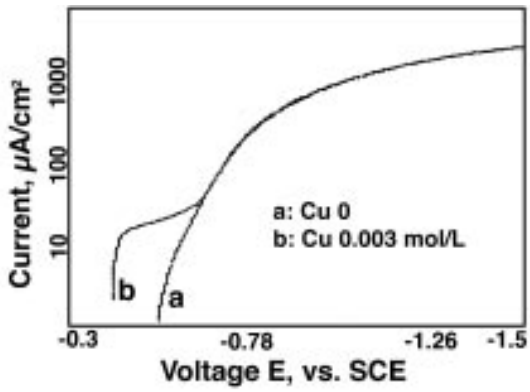

Fig. 1—Cathodic polarization.

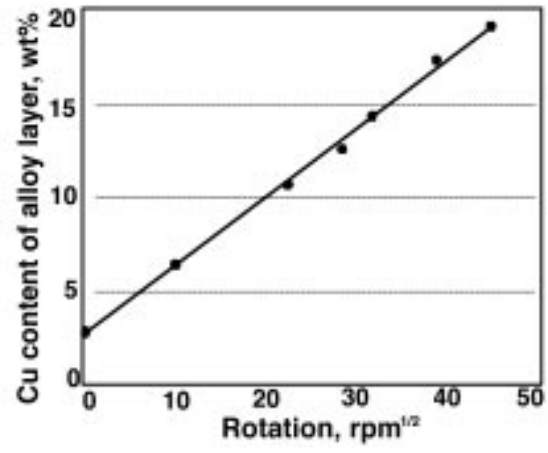

Fig. 2—Copper content of alloy layer.

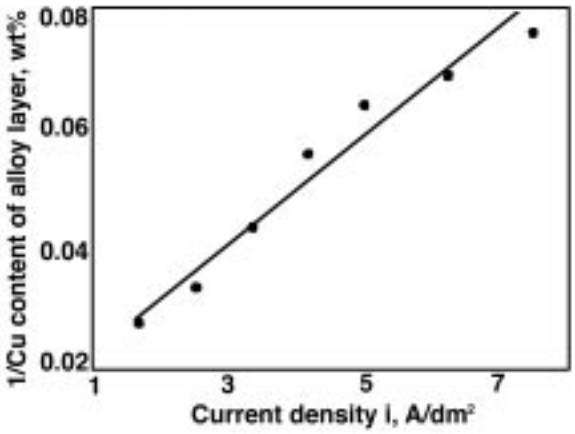

Fig. 3—Reciprocal of copper content of alloy layer vs. current density of cobalt deposition.

Levich equation:[7]

$$X_{Cu} = D_{Cu}C_{Cu}/(D_{Cu}C_{Cu} + D_{Co}C_{Co})$$

where D_{Cu} and D_{Co} are the diffusion coefficients of copper and cobalt, and C_{Cu} and C_{Co} are the concentration of copper and cobalt in the bath. Copper content also increased with increase of rotation speed. This can be seen from the linear relationship (Fig. 2) between the copper content in the alloy layer and the square root of the rotation speed, because the limiting current density for copper deposition increased with increasing rotation speed.[8]

$$j_{Cu} = 1.24FD_{Cu}^{2/3}\omega^{1/2}\nu^{-1/6}C_{Cu}$$

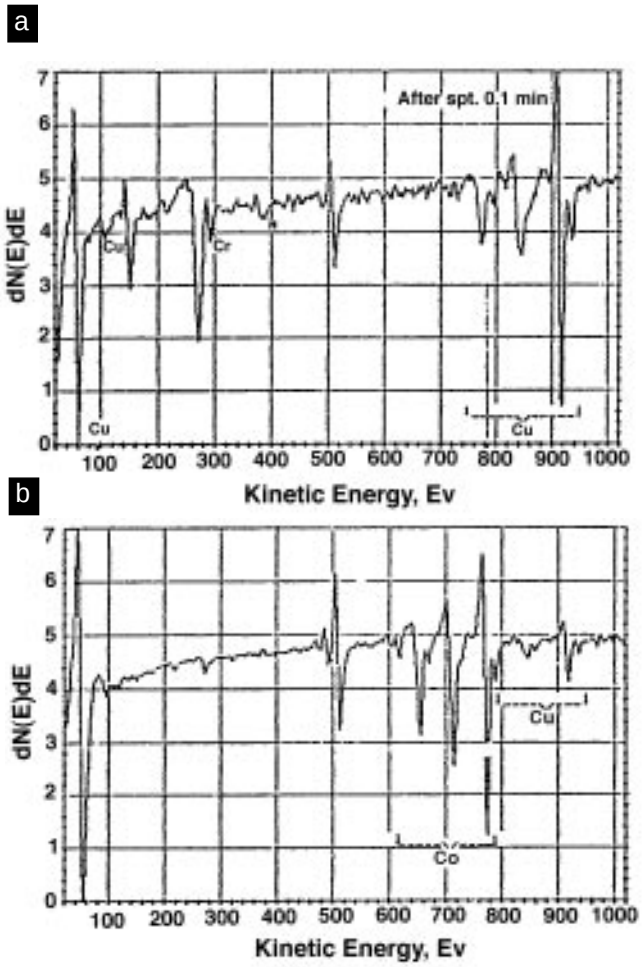

Fig. 4—Auger spectrum: (a) copper layer; (b) cobalt layer.

Next, it decreased with increase of the current density for cobalt deposition. Figure 3 shows the relationship between the reciprocal of copper content in the alloy layer and the current density for cobalt deposition. *Because* the deposition of copper is mass-transfer-controlled and the limiting current density does not change with the current density for cobalt deposition, then according to Faraday's law:

$$X_{Cu} = Ki_{Cu}/i \text{ and } 1/X_{Cu} = Ki/i_{Cu}$$

where i_{Cu} is the limiting current density for copper deposition and i is the current density for cobalt deposition.

Figure 4 shows the Auger spectrum of the multilayer film. It can be seen that the copper layer is indeed composed of pure copper; the cobalt layer is an alloy. The Auger depth profile of the multilayer film, shown in Fig. 5, reveals the thickness of the copper layer to be 15 nm and that of the cobalt layer, 20 nm. The sputtering rate is about 5 nm per minute. The results of TEM also confirmed the layered structure. The decay in wave amplitude for longer sputtering time is explained by the decrease in depth resolution resulting from surface roughness and the redeposition of sputtered atoms from valleys.[9]

Figure 6 shows the result of XRD. The results indicate the presence of two distinct phases of copper and cobalt (note the peaks at $2\theta = 74.3°$ for (220) fcc Cu and $2\theta = 75.6°$ for (220) fcc Co). The peak at 43.5° is the convolution of (111) fcc Co and (111) fcc Cu, and the peak at 50.3° is the convolution of (200) fcc Co and (200) fcc Cu. This indicates that the growth of copper on cobalt and the growth of cobalt on copper are epitaxial.

Conclusions

1. Cu/Co multilayer film can be produced by electrodeposition from the following electrolyte: 0.003-0.01 mol/L $CuSO_4 \cdot 5H_2O$, 0.035 mol/L $CoSO_4 \cdot 7H_2O$ and 50-70 mL/L additive; pH 5-7.
2. The multilayer film possessed distinctly layered structure. It consisted of a pure copper layer and a cobalt-copper alloy layer.
3. The copper content of the alloy layer increased with increasing concentration of copper ions in solution and with increase of rotation speed.

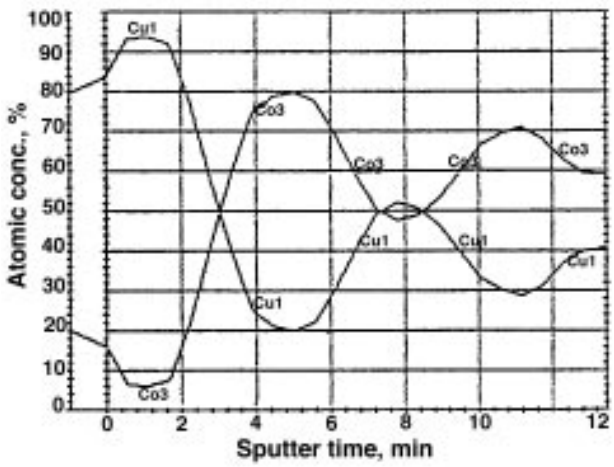

Fig. 5—Auger depth profile of multilayer film.

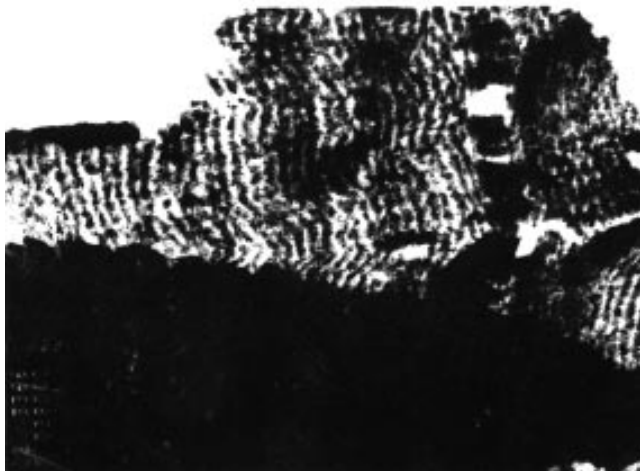

Fig. 6—X-ray diagram of Cu/Co multilayer film.

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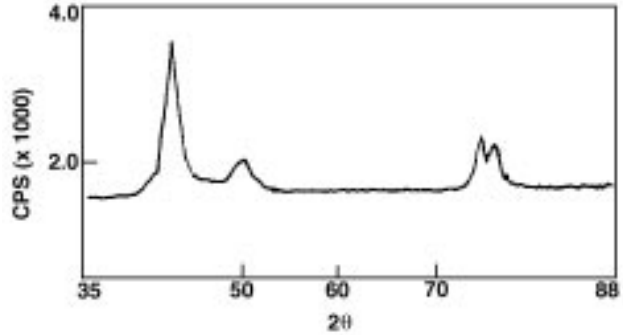

Fig. 7—TEM photomicrograph of deposit cross section.

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