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Magnetoresistance of Electrodeposited Co/Cu Multilayer Nanowires

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Co/Cu multilayer nanowires were electrodeposited potentiostatically on highly ordered porous anodic alumina oxide templates. Scanning electron microscopy (SEM) showed that wires have diameters of about 250–300 nm and length of 40–50 μm. Co/Cu multilayer nanowire arrays embedded in anodic alumina oxide were mechanically polished with diamond in a suspension of oil until the wires appeared. Then the top and bottom surfaces of the material were coated with a layer of Au with a thickness of 100 nm for electrical contacts. Magnetic field was applied by an electromagnet and resistance was measured by four point technique.

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1. Introduction

The magnetoresistance (MR) effect is the variation of the electrical resistance of a magnetic material under the effect of an external magnetic field. The MR of magnetic nanowire arrays has been studied intensively in the last twenty years. MR effect has been used widely in magnetoresistance sensors, which found applications in measurement or detection of magnetic field.

One-dimensional nanowires with large aspect ratio have received much attention due to unique shape anisotropy and extremely large surface area [1, 2]. The characteristic magnetic properties of magnetic nanowires can be controlled by choice of material and dimensions [3]. MR effect is observed in magnetic multilayered nanowires when the ferromagnetic elements are layered with nonmagnetic elements [4]. MR characteristics are highly dependent on the composition and thickness of deposited layers. Electrodeposition technique of multilayers has advantages with respect to complex vacuum deposition techniques in terms of cost and growth rate. Electrodeposited Co/Cu [4], CoFe/Cu [5], NiFe/Cu [6], CoNiFe/Cu [7], multilayer nanowires are potential candidates for magnetic sensors [4], biosensors [8], current sensor [9], linear and rotational position sensor [10], head recording [11], spintronic sensor [12].

In this study, we obtained CoCu and Co/Cu multilayer nanowires in highly ordered porous anodic alumina oxide (AAO) templates by DC pulsed electrodeposition from sulfate bath. The magnetoresistance properties of electrodeposited Co/Cu nanowires were also investigated.

2. Experimental

All solutions were prepared by dissolving reagent-grade chemicals in deionized water of Milli-Q quality. The volume of the electrochemical bath was approximately 50 ml. The single sulfate bath contained a mixed solution 0.2 M $CoSO_4{\cdot}7H_2O$, 1–10 mM $CuSO_4{\cdot}5H_2O$, 0.2 M H_3BO_3, and 35 mM Na_2SO_4. Electrodeposition into the pores was carried out in a three-electrode cell. An Ag/AgCl electrode (BAS, 3 M NaCl, and −35 mV versus SCE at 25 °C) was used as the reference electrode. A platinum electrode approximately 5 times larger than the cathode was used as an auxiliary electrode. Anodic alumina oxide (AAO) membranes, with specified pore diameter of 200 nm and pore length of 200 μm, were used as the cathode for the nanowire synthesis. These have an exposed area of approximately 1 cm^2. Before the electrodeposition, back side of the AAO templates was coated with Au with a thickness of 100 nm, and an adhesive carbon disc and copper foil were also stuck on to ensure a good conductivity needed for the electrodeposition [13]. The electrodeposition of nanowires was performed by means of an electrochemical analyzer system, Iviumstat potentiostat/galvanostat. The electrodeposition was performed by pulsed electrodeposition by applying a DC potential. After the production of nanowire arrays, Co/Cu nanowire arrays embedded in AAO were mechanically polished with diamond particles in a suspension of oil until nanowires appeared.

Resistance measurements were performed with four-probe techniques. The front side of polished AAO was coated with 100 nm Au. Then electrical contacts were made on Au films on the both side of AAO using conductive silver paint. The resistance as a function of magnetic field (MR) at different DC biased current was measured in an axial magnetic field at room temperature. The MR ratio was calculated from the following equation:

$$\frac{\Delta R}{R}(\%) = 100 \times \frac{[R(H) - R(H_{\max})]}{R(H_{\max})}, \tag{1}$$

where $R(H_{\max})$ is the resistance measured at a magnetic field of $H \approx 1$ T. In MR measurements the magnetic field was applied perpendicular and parallel to AAO surface, using an electromagnet. The perpendicular direction to AAO surface plane corresponds to the parallel direction

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to the long axis of nanowires.

The surface properties of nanowire arrays were investigated by scanning electron microscopy (SEM; LEO-EVO-40) and transmission electron microscopy (TEM; FEI Tecnai G2 F30). The quantitative chemical analyses of the alloys were performed by energy dispersive X-ray (EDX) spectroscopy.

3. Results and discussions

Figure 1a shows cyclic voltametry curve of Cu, Co, Cu-Co during deposition on AAO. The *CV* curves show that there are three reaction regions corresponding to cathodic deposition, no reaction and anodic oxidation processes. On both the positive and negative sweeps of curves, cathodic currents are clearly found, indicating that copper and cobalt ions can be deposited into the AAO templates. Anodic currents can be attributed to the dissolution of already deposited metal atoms. The cyclic voltammograms of electrolyte containing Cu, Co and Co-Cu at 10 mV/s indicated that the nucleation and growth onset of Cu, Co, Co-Cu begins above 0.05 V, −0.045 V and 0.033 V, respectively. When the potential scan direction was reversed, dissolution onset of Cu, Co, Co-Cu begins above −0.59 V, −0.65 V and −0.733 V, respectively. Then we chose the deposition potentials as −0.5 V for Cu and −1.5 V for Co. A potential pulse oscillating between −0.5 and −1.5 V vs. Ag/AgCl was employed for electrodeposition of the Co-Cu nanowires inside the AAO (Fig. 1b). Figure 1c shows that growth of the nanowires was often not a steady-state process, and it appears that there was significant current oscillation as voltage was applied to the cathode. According to the current versus time plot, pore filling time was around 37500 s.

The general morphologies of the electrodeposited Co/Cu nanowires obtained inside the pores of the AAO were studied by SEM (Fig. 2a, 2b). The electrodeposited nanowires are parallel, aligned regularly and densely distributed. The top-view SEM image shows that the nanowires are of the same radius and shape as AAO. TEM images of multilayered nanowires at various pulsed deposition potential times are obtained after complete dissolution of AAO in 1 M NaOH solution. The feature of Co segments alternated with Cu layers is clearly seen in Fig. 2c–2f, where the pulse time of copper was varied between 20 s and 2 s, while the cobalt pulse time was constant 10 s. The effect of the decrease in pulse time of copper on the nanowire morphology results in an increase in the number of copper layers in nanowires. EDS spectra were obtained from points 1 and 2 (Fig. 2d). It was found that point 1 has rich Co content and poor Cu content, on the other hand point 2 has rich Cu content and poor Co content.

Figure 3 shows MR curves for Co/Cu multilayered nanowire arrays embedded in AAO. Resistance of the nanowires gradually increases with the decreasing magnetic field. It should be noted that the variation in the pulse duration leads to a change in the shape of MR curve. The maximum MR change of 0.55% was observed

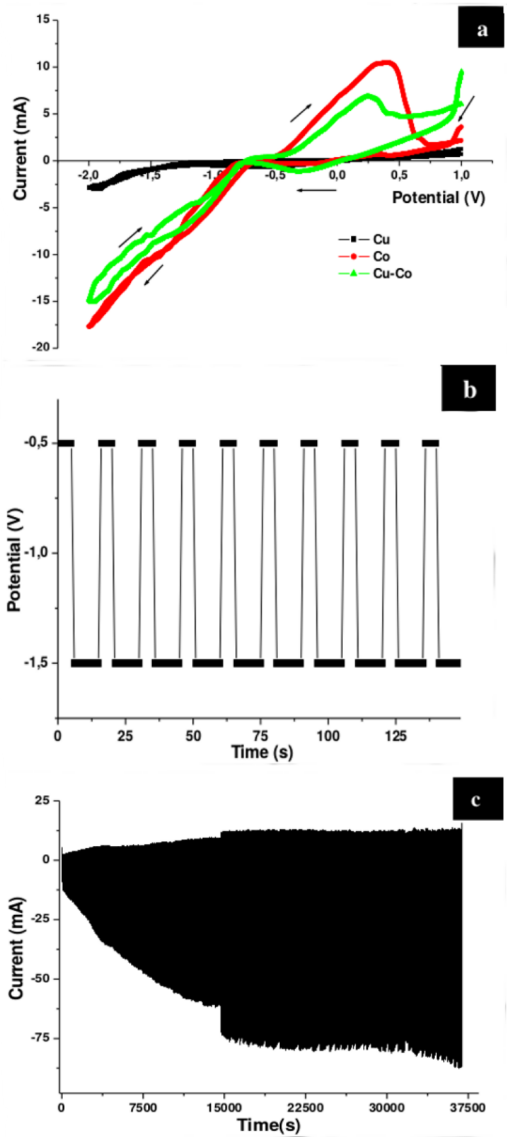

Fig. 1. (a) Cyclic voltammograms of Co-Cu at 25 mV/s from solution of 0.2 M $CoSO_4{\cdot}7H_2O$, 1 mM $CuSO_4{\cdot}5H_2O$, 0.2 M H_3BO_3, and 35 mM Na_2SO_4. (b) Time waveform of the pulse electrodeposition, where deposition times of Cu and Co are 5 s and 10 s, respectively. (c) Current transient curve of pulse plated Co/Cu multilayered nanowires.

in nanowire arrays for which the pulse time was 2 s for Co and 10 s for Cu (Fig. 3a). It was also observed that double peak behavior centered at origin for the sample nanowire, for which the pulse time was 5 s for Co and 10 s for Cu.

4. Conclusions

In this paper, we have employed the pulsed electrodeposition technique to obtain Co/Cu multilayer nanowires, in which layer thickness is tuned by applying electrodeposition potential having various pulse times.

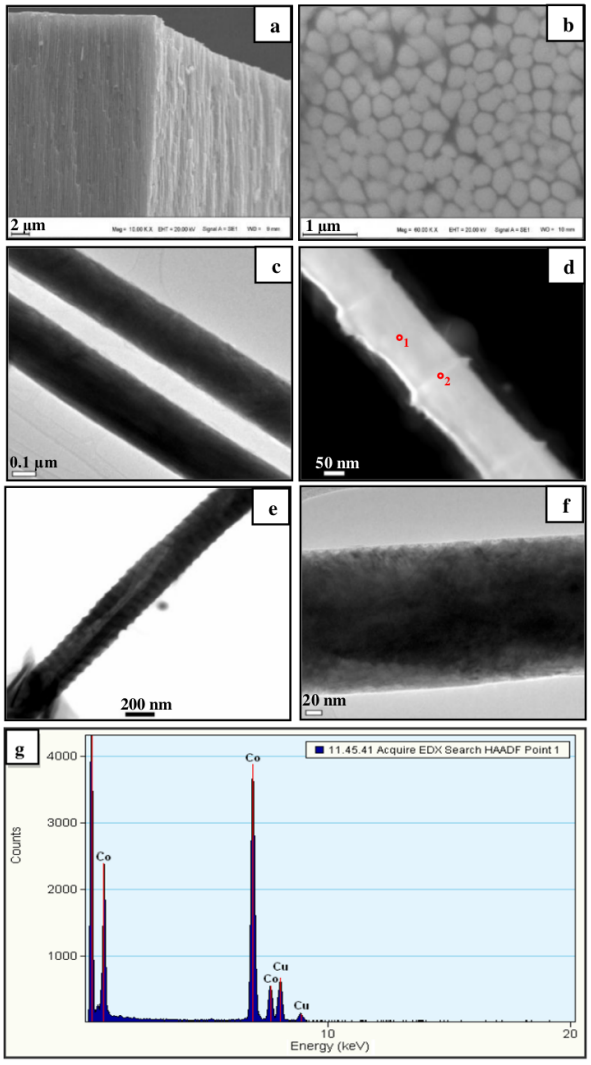

Fig. 2. (a) Cross section SEM images of AAO template filled with nanowires. (b) Top view SEM image of mechanically polished alumina membrane filled with nanowires. (c)–(f) TEM images of ordered Co/Cu nanowires for various electrodeposition pulse delay times, after liberation from AAO. (g) The EDS of spectrum for nanowire from figure (d).

The pulsed electrodeposition method provides a simple and cheap way to obtain multilayered nanowire arrays. The structure and magnetic characteristics of multilayer nanowires strongly depend on various parameters, like electrolytic bath content and concentration, pH and temperature, as well as time and potential of the electrodeposition potential. The maximum value of MR ratio of about 0.55% was obtained for the nanowires array deposited at pulse time of 2 s for Co and 10 s for Cu.

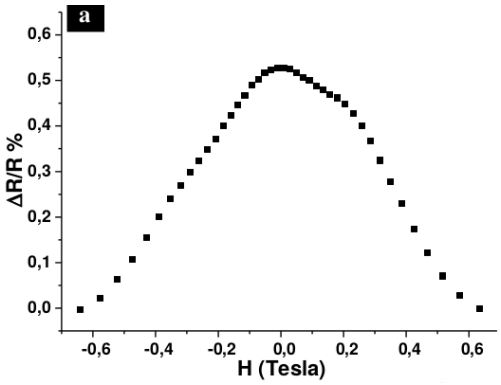

Fig. 3. Magnetoresistance curves obtained for arrays of Co/Cu nanowire arrays at for various electrodeposition pulse times. The field applied along the wire axis.

Acknowledgments

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