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Controlled Cu content of electrodeposited CoCu nanowires through pulse features and investigations of microstructures and magnetic properties

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ABSTRACT

CoCu alloy nanowire arrays embedded in anodic alumina template were fabricated by ac pulse electrodeposition. Different off-times between pulses in an electrolyte with constant concentration of Co^{+2} and Cu^{+2} and acidity of 4 were employed. The effect of deposition parameters on the alloy contents, microstructures and magnetic properties of Co_xCu_{1-x} nanowires were studied. It is shown that Co content decreased by increasing the off-time between pulses in a wide range (x = 0.53–0.07). These results are in consistence with saturation magnetization, which was reduced with increase in the off-time between pulses. It was also found that by optimizing the off-times, it is possible to fabricate CoCu nanowires with mixed phase of hcp Co, fcc Cu and fcc CoCu crystal phase.

1. Introduction

Porous aluminum oxide was used as attractive template material to fabricate nanowires because of its high pore density, small pore diameter and uniform pore distribution [1]. Fabrication of nanowire arrays has become the subject of intensive study due to their applications in the high-density magnetic storage devices and for magnetic sensors [2–5]. Numerous magnetic metals and magnetic alloys such as Co, Ni, Fe, FeNi and CoFe have been prepared through electrodeposition into self-assembled anodic aluminum oxide templates [6–8,3].

Non-magnetic substances added in magnetic nanowires have been shown to be conventional method to control the magnetic properties of the nanowire arrays. So far, many non-magnetic elements have been added in the magnetic nanowire arrays such as Cu [9], Pd [10], Pt [11,12], and Pb [13]. The magnetic properties of Co-based nanowires have been more interested than the single phase nanowires, since more grain surfaces and boundaries can develop the effective anisotropy and increase the magnetic coercivity. In the survey of magnetic nanowire arrays [9,14] magnetic–non-magnetic alloys such as CoCu have been reported for exhibiting particular magnetic characters. Although very few studies have been found on the fabrication and characterization of CoCu nanowires, most investigations focus on Co/Cu multilayer nanowire arrays [15,16]. The arrays of multilayered nanowires appeared as an useful mean to study giant magnetoresistance (GMR) effects [17–19]. Studies of the magnetostatic coupling effects of the magnetic layers have found basic advances in magnetic models.

Although due to complicated physical magnetization reversal in CoCu nanowires fewer researches have been carried out in this area some highlighted works were sampled. A coercivity of 244 Oe is reported in dc electrodeposited $Co_{0.77}Cu_{0.23}$ nanowires embedded in anodic aluminum oxide template with a 30 nm pores diameter [14]. In another noteworthy research, the magnetic properties of dc electrodeposited CoCu nanowires were investigated using different voltages and acidities [9].

In the present work, CoCu nanowires embedded in porous aluminum oxide templates were fabricated using pulse electrodeposition technique. The influence of off-time between pulses on the microstructures and magnetic properties of the nanowires was investigated. One valuable view of this research is a simple method of electrodeposition in which we are able to fabricate CoCu alloy nanowires with a certain composition. This method also enables us to establish the optimize conditions to fabricate Co/Cu multilayered nanowires.

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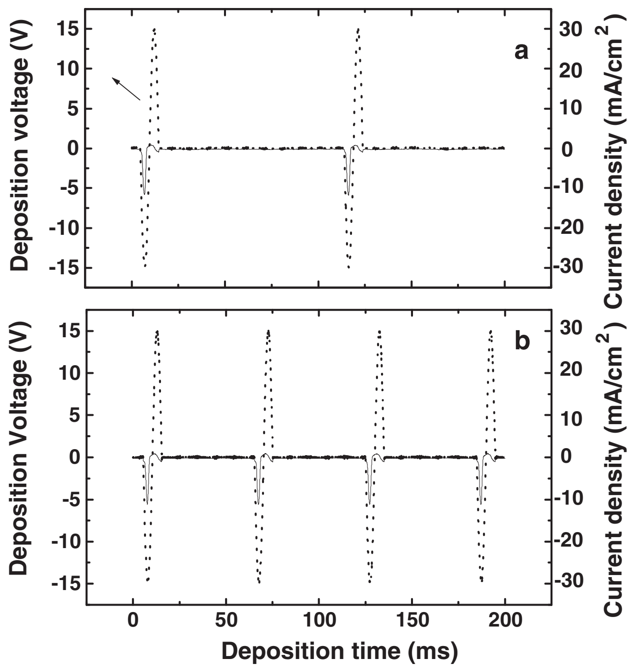

Fig. 1. A typical voltage and deposition current curve as a function of time for (a) 20 ms off-time and (b) 200 ms off-time.

2. Experiments

Anodic aluminum oxide (AAO) templates were prepared by two-step anodization process as reported elsewhere [20]. Co_xCu_{1-x} alloy nanowires were electrodeposited into self-assembled nanoporous templates with electrolyte solution of 0.75 M $CoSO_4{\cdot}7H_2O$, 0.05 M $CuSO_4{\cdot}5H_2O$ and 45 g l^{-1} H_3BO_3. Acidity of as prepared solution was in the range of 3.3–3.5, which increased to 4 by adding NaOH. The electrolyte temperature was 30 °C. Pulse electrodeposition was carried out using sine waveform with same reductive/oxidative voltages of 15/15 V. The reduction/oxidation time of all the samples was 5 ms, while the off-time between pulses were 10, 20, 50, 100, 200 and 250 ms. A schematically sine waveform with different off-times is shown in Fig. 1. The alloy composition of the samples was determined by energy dispersive spectroscopy (EDS). An alternating gradient force magnetometer (AGFM) was used to measure the magnetic properties of nanowires at room temperature. The crystalline structure of the nanowire arrays was examined by X-ray diffraction (XRD). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to confirm the morphology of the samples.

3. Result and discussion

A cross sectional view of the nanowires array is displayed in Fig. 2. A top view AFM image is also inserted. From this figure an almost ideally arranged hexagonal cell configuration was observed with an interpore distance and pore size of approximately 104 and 30 nm, respectively.

Although Co and Cu concentrations in electrolyte solution were modified through Nerenst's relation to equalize the Cu^{+2} and Co^{+2} ions reduction, the EDS analysis evinced that the electrodeposition rate of Cu^{+2} and Co^{+2} ions was not the same. As shown in Fig. 3(a), the amount of Cu content in nanowires has been enhanced from 47% to 93% when the off-time between pulses increased from 10 to 200 ms. One could see that increasing the off-time between pulses increases Cu content in CoCu alloy nanowires. Results are consistent with the saturation magnetization of these nanowires, which

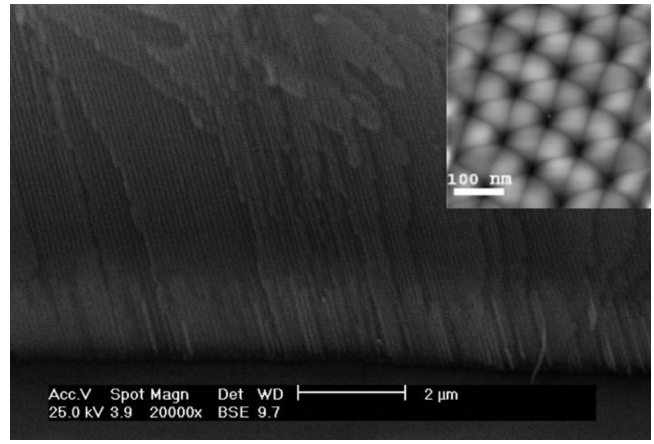

Fig. 2. A SEM cross sectional view of CoCu nanowire arrays. A top view AFM image of alumina template prepared by two-step anodization technique is also inseted.

achieved by analysis of magnetic measurements of samples, shown in Fig. 3(b). Control of electrolyte solution and off-times between pulses enable us to fabricate Cu-rich and Co-rich nanowires, which is a simple way to prepare Co/Cu multilayer nanowires. Since considerable reduction of Co occurs in nanowires fabricated at 250 ms off-time, there is no precise analysis of magnetic measurement of the CoCu nanowire arrays prepared by this off-tim. It seems that in the reduction time Cu^{+2} and Co^{+2} ions were reduced but in the period of off-time Co atoms, considering their very low standard potential in comparison with that in Cu (standard potential of Cu is equal to 0.347 V while it is −0.277 V for Co), are replaced with Cu through electroless process. Increasing off-time enhances the replacement of Co atoms with Cu^{+2} ions. Considering this fact, at a certain reduction-oxidation time CoCu nanowires containing a wide range of Cu non-magnetic element (0.47–0.93) were prepared. The variations of the longitudinal coercivity as a function of off-time were determined with the external field applied along the wires axis. Magnetization measurements were carried out at

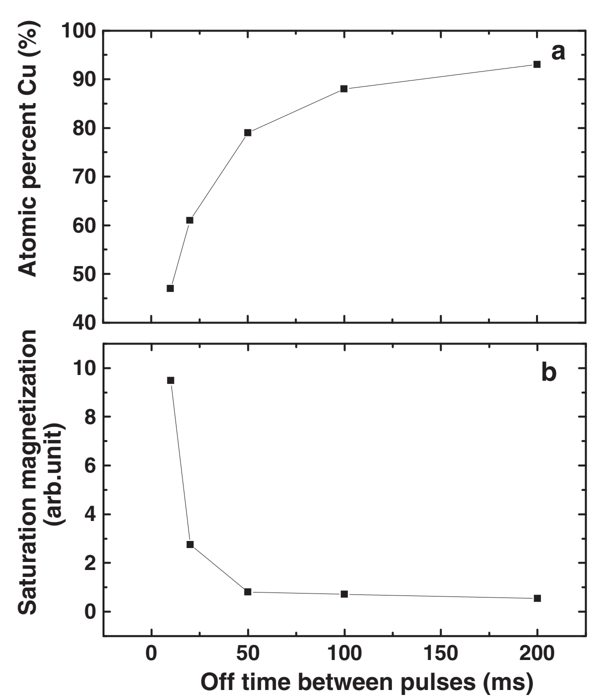

Fig. 3. (a) Atomic percent of Cu and (b) saturation magnetization of CoCu nanowire arrays as a function of off-time between pulses.