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Fabrication of CoZn alloy nanowire arrays: Significant improvement in magnetic properties by annealing process

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ABSTRACT

Highly ordered arrays of $Co_{1-x}Zn_x$ ($0 \le x \le 0.74$) nanowires (NWs) with diameters of ~35 nm and high length-to-diameter ratios (up to 150) were fabricated by co-electrodeposition of Co and Zn into pores of anodized aluminum oxide (AAO) templates. The Co and Zn contents of the NWs were adjusted by varying the ratio of Zn and Co ion concentrations in the electrolyte. The effect of the Zn content, electrodeposition conditions (frequency and pH) and annealing on the structural and magnetic properties (e.g., coercivity (Hc) and squareness (Sq)) of NW arrays were investigated using X-ray diffraction (XRD), scanning electron microscopy, electron diffraction, and alternating gradient force magnetometer (AGFM). XRD patterns reveal that an increase in the concentration of Zn ions of the electrolyte forces the hcp crystal structure of Co NWs to change into an amorphous phase, resulting in a significant reduction in Hc. It was found that the magnetic properties of NWs can be significantly improved by appropriate annealing process. The highest values for Hc (2050 Oe) and Sq (0.98) were obtained for NWs electrodeposited using 0.95/0.05 Co:Zn concentrations at 200 Hz and annealed at 575 °C. While the pH of electrolyte is found to have no significant effect on the structural and magnetic properties of the NW arrays, the electrodeposition frequency has considerable effects on the magnetic properties of the NW arrays. The changes in magnetic property of NWs are rooted in a competition between shape anisotropy and magnetocrystalline anisotropy in NWs.

1. Introduction

Fabrication of metal NWs has attracted a lot of interest due to their potential applications in high-density storage media [1], highly sensitive giant magnetoresistance (GMR) materials [2], sensors [3], biosensors [4], photocatalysts [5], thermoelectric cooling systems [6], and photonic crystals [7]. NWs have been fabricated using different methods such as chemical vapor deposition [8], electroless growth [9], and electrodeposition [10]. Among different electrodeposition methods, template-assisted techniques appear to be promising due to simplicity and the high level of control over the morphology, microstructural properties, packing density, size, and physical properties of NWs by tuning the template and electrodeposition parameters. In comparison to DC methods, AC electrodeposition requires a less complex sample preparation process and leads to higher filling factor, which is very important for practical applications. Single element magnetic NWs of Co [10], Fe [11] and Ni [12] have been electrodeposited and extensively studied. Many attempts have also been focused on the fabrication of NW alloys in order to improve the magnetic and mechanical performances of the NWs for practical application and to study the fundamental mechanisms behind the magnetic properties of these materials. For the case of Co, different NW alloys of ferromagnetic elements such as CoFe [13] and CoNi [14] as well as ferromagnetic/non-ferromagnetic alloys such as CoLa [15], CoPd [16], CoPt [17], CoGd [18], CoP [19], CoAg [20], CoCr [21], $CoSi_2$ [22], CoCu [23], CoNiP [24], CoNiPb[25], CoFeTb [26], CoZnP [27] have been reported. While there are many reports in the literature for fabrication of CoZn bulk and thin film alloys, however, to the best our knowledge only one report has reported fabrication of CoZn alloy NWs [28]. In this work, we investigate the magnetic properties and crystal structure of high length-to-diameter ratio arrays of CoZn NW alloys. The effect of Zn concentration, annealing, electrodeposition conditions (e.g., frequency and electrolyte pH) on the crystal structure and magnetic properties of CoZn NW alloys are systematically investigated.

2. Experimental procedure

2.1. Preparation

CoZn NW arrays were fabricated using electrodeposition and template method. AAO were made by anodizing the aluminum foils

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in a conventional two-step process [29]. Discs with 8 mm in diameter and 0.4 mm thick of high purity (99.999%) aluminum were ultrasonically degreased in acetone followed by annealing at 450 °C for 1 h in high purity Ar. Samples were then etched in 3 M NaOH at room temperature for about 3 min for removing the oxide layer prior to an anodization process. Samples are then washed and electropolished in 1:4 (v/v) solutions of perchloric acid and ethanol at 25 °C. Conventional two-step mild anodization process is employed to obtain highly ordered with high aspect ratio pores. The first anodization is carried out in 0.3 M oxalic acid electrolyte at 40 V and 17 °C for 15 h with 23 mm distance between anode and cathode. The anodized layer was then removed by immersing the samples to a solution containing 0.2 M chromic acid and 0.5 M phosphoric acid for 15 h at 70 °C. The second anodization is carried out at the same conditions for 1 h. The thickness of barrier layer is estimated to be about 40 nm since barrier layer thickness is reported to be about 1 nmV^{-1} [30]. This barrier layer is too thick for electrodeposition process due to its high resistivity, and thus needs to be thinned. The thinning process was performed by decreasing the anodization voltage in three stages as shown in Fig. 1. In the first stage, the anodization voltage was decreased by 2 V min^{-1} from 40 V to 20 V. The anodization voltage then decreased from 20 V to 10 V in the rate of 1 V min^{-1} followed by decreasing to 8 V with the rate of 0.5 V min^{-1}. At the end, the anodization process was continued for 3 min at 8 V in order to obtain uniform barrier layer. The final thickness for barrier layer is estimated to be about 8 nm.

CoZn NW alloys were then prepared by co-electrodeposition of Co^{+2} and Zn^{+2} ions in the AAO pores at room temperature. AC sine wave (30 V_{pp}) was used for electrodeposition. A solution of $(1-y)$ M $CoSO_4{\cdot}7H_2O + y$ M $ZnSO_4{\cdot}7H_2O$ and 30 gl^{-1} boric acid was used as the electrolyte. The Zn content of the NWs was adjusted by varying y. At the beginning the pH value of the electrolyte was about 3.2, but it was adjusted to 4 and maintained constant during the experiment with NaOH. The electrolyte was continuously agitated during the deposition procedure.

2.2. Characterization

Morphology of samples was studied by scanning electron microscope (SEM) and transmission electron microscope (TEM). Magnetic properties of the NWs embedded in the AAO templates were measured by an alternating gradient force magnetometer (AGFM). The crystal structure and composition of NWs were characterized by XRD and electron diffraction (EDX), respectively.

3. Results and discussions

3.1. Anodization current and voltage

Fig. 1 shows a typical anodization current and voltage during the second anodization and barrier layer thinning process. The barrier layer thinning is performed at the final stage of anodization process by decreasing the anodization voltage as shown in the figure. As seen, during the thinning process the anodization current abruptly drops by decreasing the voltage at each step then levels to a constant value.

3.2. Morphology

Fig. 2(a) shows a typical top view SEM micrograph of a pore structure after the second anodization process. As seen pores are well distributed in the hexagonal pattern, which is an ideal pattern for anodized AAO. The average pore diameter and spacing are about 37 nm and 100 nm, respectively. A typical cross-sectional SEM micrograph of as prepared AAO is displayed in Fig. 2(b), which displays high aspect ratio parallel cylindrical nanopores without intercrossing. Fig. 2(c) shows the TEM image of the NWs released from the AAO template. To release the NWs from the AAO templates the electrodeposited membranes were dissolved in the solution containing 0.2 M chromic acid and 0.5 M phosphoric acid. NWs are then washed several time by distilled water and dispersed in methanol. The diameter of as-synthesized NWs is almost the same as AAO pore diameter. The sharp contrast along the NWs shows polycrystalline properties of NWs. The length of NWs varies from 1 μm up to 5 μm depending on the electrodeposition time. Therefore, NWs have an aspect ratio ranging from 30 to 150. Arrays of NWs with aspect ratio of about 60 were prepared for further magnetic and microstructure characterization.

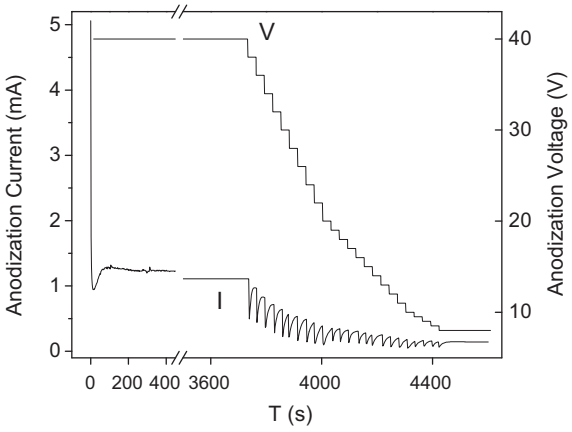

Fig. 1. A typical anodization current and voltage during the second anodization and barrier layer thinning process.

3.3. Co and Zn content

The quantitative EDX analysis reveals that Co and Zn content of as deposited NWs depend on the ionic concentrations of Co^{2+} and Zn^{2+} in the electrolyte. Six group of samples were prepared using the solution of $(1-y)$ M $CoSO_4{\cdot}7H_2O + y$ M $ZnSO_4{\cdot}7H_2O$ with $y = 0$, 0.01, 0.05, 0.10, 0.15, and 0.20 as electrolyte. Samples were AC electrodeposited by a sine wave, $V_{pp} = 30$ V and $f = 200$ Hz. The pH of the electrolyte was adjusted to 4 and maintained constant during the electrodeposition procedure at room temperature. A typical EDX result of NW arrays is shown in Fig. 3, displaying the presence of Co and Zn in the NWs. Inset to this figure summarizes the variation of Zn content (obtained by EDX) in the as prepared NWs versus the molar concentration of Zn in the electrolyte. As seen the Zn content in the NWs has a nonlinear relation to the ionic concentration of Zn in the electrolyte (0.3, 0.11, 0.24, 0.46, and 0.74 corresponding to $y = 0.01$, 0.05, 0.10, 0.15, and 0.20, respectively). The amount of Zn in the NWs rapidly increases with increasing the Zn^{+2} concentration in the electrolyte, revealing that Zn is deposited much faster than Co due to anomalous co-deposition, which was described as of the preferential deposition of the element with less positive standard electrode potential and was investigated before [31,32]. This is in contrast to the normal co-electrodeposition of alloys such as CoFe, where the NW content of each element is proportional to the corresponding ionic concentration in the bath [13,33]. It should be noted that the amount of Co content in the NWs is significantly low for higher y values, about 26 at% for sample electrodeposited using the electrolyte with $y = 0.2$.

3.4. Effect of the Zn content

The effect of the Zn content on the magnetic properties of NW alloys was investigated by performing magnetization measurements at room temperature. Fig. 4 shows typical normalized