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Conversion of magnetic anisotropy in electrodeposited Co–Ni alloy nanowires

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ABSTRACT

In this paper, the influence of alternating current (ac) electrodeposition frequency and waveform is reported on chemical composition, microstructure and consequently magnetic properties of Co–Ni binary alloy nanowire arrays embedded in an alumina template. For sinusoidal and square electrodeposition waveforms the easy axis of magnetization rotates from being parallel to perpendicular orientation to nanowire long axis as the deposition frequency increases from 200 to 800 Hz. The reason for the drastic change of magnetic anisotropy in nanowires is attributed to the increase of cobalt content and the crystal structure phase transformation from *fcc–hcp* mixture at high Ni content to *hcp* at high Co content. We explain the conversion of magnetic behavior of nanowire arrays in terms of a competition between the shape and magnetocrystalline anisotropies.

1. Introduction

MAGNETIC nanowires (NWs) as a major category of nanostructures have attracted great interest for many applications such as electronics, magnetics and devices [1,2]. Compared with physical methods such as nanolithography and other model methods, these nanowires can be readily and effectively synthesized using chemical and electrochemical techniques [3]. Electrochemical deposition is a simple and cheap method to produce NWs. Nanowires with a high length to diameter ratio can be grown into porous membranes such as anodic aluminum oxide (AAO) [4,5].

Template electrodeposition using direct current (dc) is known as a traditional way to fabricate a range of compositions and structures in magnetic NWs. However, it requires the templates to become conductive in a distinct process. In contrast, ac electrodeposition enables direct deposition of NWs into AAO. In this technique, ac current factors including amplitude, frequency and waveform have significant effects on the growth and properties, though; so far little work has been carried out in this field. Magnetic properties and microstructures of magnetic Co nanowires can be controlled by adjusting the deposition parameters [6]. Usually electrodeposition of Co nanowires leads to a polycrystalline structure with wires having many grains with random c-axis orientation [7]. Many works have been done to rotate the *c*-axis of *hcp* Co grains parallel or perpendicular to the nanowire axis [8–11]. As a result, transformation of crystal structure in nanowires changes the magnetic behavior which is driven by the effective magnetic anisotropy K_{eff} depending on competition between the shape and magnetocrystalline anisotropies. One possibility to tune K_{eff} is to produce binary alloy nanowires of cobalt and nickel [12–16]. Nanowires with tailored crystal structures can be produced by variation of electrodeposition conditions mainly through an adjusting of bath pH and/or temperature, amplitude of electroplating current, aspect ratio of template pores, amplitude and orientation of an external magnetic field during electrodeposition [11,17–19]. A little attention has been paid to tune the crystal structure of nanowires by variation of frequency and waveform of electrodeposition current. This paper aims to understand the magnetic behavior of cobalt-based binary nanowires by the addition of nickel as an alloying element controlled by ac parameters.

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2. Experimental

Co–Ni NWs were produced by ac electrodeposition into AAO template. We used two-step anodization technique to prepare AAO as completely described in [4,5]. Anodization was conducted for 6 h at each step at 40 V in 0.3 M oxalic acid. In order to modify AAO templates, the thickness of the barrier layer at the bottom of the pores was decreased by step-wise reduction of the anodizing voltage at the end of the second stage of anodization. Electrodeposition bath containing 28 g/l $CoSO_4{\bullet}7H_2O$, 72 g/l $NiSO_4{\bullet}6H_2O$ and 30 g/l H_3BO_3 was prepared by dissolving reagent grade chemicals in deionized water. Ac electrodeposition under constant voltage amplitude was conducted. Two-electrode electrodeposition cell was used consisting of an ac function generator as the power source connected to computer through an A/D data acquisition card to apply and control a range of deposition frequency from 200 to 800 Hz, voltage amplitude (18 V) and waveforms (sinusoidal and square). Voltage amplitude was maintained constant under the conditions of this study as the four stage of growth of NWs in AAO template could be readily achieved.

Transmission electron microscopy (TEM ARM200F, JEOL), scanning electron microscopy (SEM Supra, Carl Zeiss), X-ray diffraction (XRD-Brucker, using the incident Cu Kα radiation (1.54 Å)) technique, energy dispersive X-ray analysis (EDX Oxford Inst.) and atomic force microscopy (Ntegra Aura, NT-MDT) were used to examine the morphology and structure of electrodeposited NWs. Magnetic properties of Co–Ni NWs were defined according to magnetization curves measured using the highly sensitive home-made vibrating sample magnetometer (VSM) in magnetic field range ± 3 kOe. Integral magnetization measurements were carried out at room temperature. The magnetic hysteresis loops were measured by rotation of samples with a step of 10° with respect to the direction of the applied field in the interval of 0–360°. The external magnetic field was applied in-plane of the alumina template and rotated toward the perpendicular to the plane direction with a step of 10° (NWs axis is perpendicular to the plane of the template). From the hysteresis loops we determined the normalized remanence M_r/M_s (where M_r is remanent magnetization at zero field, M_s is saturation magnetization) and coercive force H_c.

3. Results and discussion

3.1. Composition and microstructure

Co–Ni nanowires were electrodeposited into AAO templates with an average pore diameter of 40 ± 2 nm and length of 4 ± 0.2 μm and an interpore distance (from center to center) of 100 ± 4 nm. Size distribution histograms of AAO templates were obtained on SEM images. A typical SEM image of AAO template consisting of top and cross-sectional views is shown in Fig. 1. SEM shows that NW arrays have near hexagonal distribution of pores on short-range order only. The areas with hexagonal arrangement are disoriented in respect to each other. The formation of such arrangement has been precisely described in previous reports [4,5] for estimation of areas of highly ordered regions.

TEM microscopy (Fig. 2a) on isolated NWs confirmed the diameter and quality of nanowires. Using electron energy-loss spectrometry (EELS) with atomic-level chemical analysis resolution, the uniformity of atomic-levels distribution of both Co and Ni was observed on EELS maps confirming the formation of Co–Ni binary alloy instead of Co and Ni segregated phases, Fig. 2b. Selected area electron diffraction (SAED) revealed that crystal structure of NWs has a preferred plane orientation (texture) in dependence on the Co–Ni alloy composition. SAED pattern for NWs electrodeposited

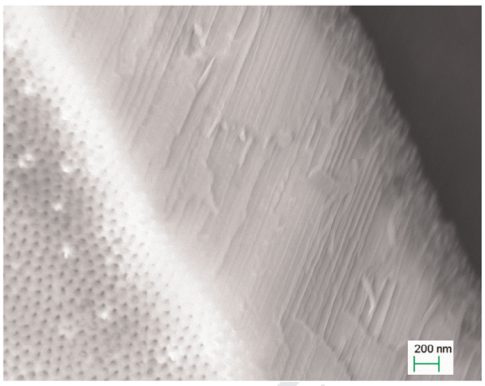

Fig. 1. SEM image of the porous AAO template with the cross-sectional view of pores filled with Co–Ni NWs at 18 V, 800 Hz, sinusoidal waveform.

at $f=800$ Hz shows hexagonal symmetry (inset in Fig. 2a), indicating that wires are polycrystalline with *hcp*-phase texture having *c*-axis perpendicular to the wire long axis. SAED patterns of other samples also reveal that electrodeposition at lower frequencies leads to polycrystalline NWs with *fcc–hcp* phase mixture.

Fig. 3 illustrates XRD patterns of NW arrays taken while they are embedded in AAO templates. The characteristics of nickel and cobalt diffraction peaks significantly depend upon the change of electrodeposition frequency and waveform. Peaks corresponding to planes of cobalt and nickel are listed in Table 1. The formation of polycrystalline Co-*hcp* showing a texture along the [100] and [002] directions is observed for all the samples. This will have a strong effect on magnetocrystalline anisotropy. Generally, a Bragg diffraction peak appeared at about 44.7° corresponds to different crystalline scatterings coming from our complicated samples including Co (111)-*fcc*, or Ni (111)-*fcc*, Al (002) and also Co (002)-*hcp*, overlapped on each other which individually could not be easily distinguished here. However, the existence of other diffraction peaks helps one understand the crystalline phase evolution in the NW arrays. Bragg peaks related to Ni (111), Ni (220) and Co(220) indices indicate that Co–Ni crystals have also been formed under different electrodeposition conditions in *fcc* phase. It is worth mentioning that Al also contributes to 002, 022 and 103 indices not indicated on the graph coming from aluminum substrate. With decreasing of deposition frequency, the intensity of Co(100)-*hcp* peak is rising for both waveforms indicating that *hcp* phase is dominantly formed. At 800 Hz applied under the square signal, the peak (100) of *hcp*-Co disappears, but intensity of *fcc* Co–Ni peaks do not change. We explain this fact by overlapping of *fcc* Co–Ni peaks with Al, whose contribution to peak intensity does not change from sample to sample. XRD results show a major change of crystalline structure from *fcc–hcp* to *hcp* phase in Co–Ni alloy nanowires with decreasing of the electrodeposition frequency. It is worth noting that the presence of Al peaks may mislead the precise interpretation of phase evolution with frequency change.

The composition of NWs was extracted from energy dispersive spectra (EDS) and summarized in Table 2. It is generally known that EDS could be used to analyze the chemical composition of metals and alloys, while the accuracy of the composition is highly dependent on many instrumental and experimental conditions on the atomic weight percentage level. We observe a significant change in the chemical composition of the alloy system and therefore, EDS could satisfactorily be used to evaluate the properties. Composition of Co–Ni NWs is very sensitive to the electrodeposition parameters. Nickel and cobalt content depends on electrodeposition waveform. Co content increases for both waveforms. For higher electrodeposition frequencies, i.e. 800 Hz, alloys become richer in cobalt.

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