Journal of Magnetism and Magnetic Materials 349 (2014) 21–26

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Crystal anisotropy induced temperature dependent magnetization in cobalt nanowires electrodeposited within alumina template

Ajeet K. Srivastav *, Rajiv Shekhar [1]

Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

ARTICLE INFO

Article history:
Received 5 June 2013
Received in revised form
11 August 2013
Available online 26 August 2013

Keywords:
Electrodeposition
Cobalt nanowire
Alumina template
Magnetic anisotropy
pH dependent cross-over temperature

ABSTRACT

Cobalt nanowires were deposited within nanoporous alumina template by direct current electrodeposition. The effect of pH on temperature dependent hysteresis behavior and magnetic properties of Co nanowires has been analyzed and discussed in detail. The easy axis of magnetization was observed to change uniformly from parallel to perpendicular direction to the wire axis with decrease of temperature from 400 K to 5 K. The effect could be attributed to increased magnetocrystalline anisotropy at lower temperatures (e.g. 5 K). Strong pH dependence of cross-over temperature that changes from 300 K to 50 K was observed and the change was delayed with increase of pH.

1. Introduction

In the last 2 decades, remarkable progress has been made in the field of nanomagnetism to get high density nonvolatile recording with the development of new fabrication and characterization techniques. The magnetic nanowires are the potential candidate for the development of future high density magnetic data storage devices. As a consequence of the nanometer size of the ferromagnetic nanowires, each single-domain nanowire could represent one bit, depending on its magnetization state [1,2].

Nanoporous alumina templates have been extensively used for growing one dimensional nanostructures due to possible tuning of structural parameters (diameter, length, and spacing) by changing the anodization conditions [3,4]. A cost-effective and relatively scalable potentiostatic electrodeposition technique allows depositing high aspect ratio magnetic nanowire arrays within alumina templates [5,6]. The magnetization behavior of such nanowires depends largely on two dominant competing interactions: (i) the crystal anisotropy due to strong spin–orbit coupling which favors aligning of the moments in a particular crystallographic direction, and (ii) the shape anisotropy due to high aspect ratio. Cobalt nanowires with *hcp* phase structure have been of much interest because of large crystal anisotropy (magnetocrystalline anisotropy constant, $K_{mc} = 5 \times 10^6$ erg/cm^3) comparable to shape anisotropy ($K_{sh} = \pi M_s^2 = 6 \times 10^6$ erg/cm^3) [7]. Depending on the easy axis direction (*c*-axis) of *hcp* phase, the magnetocrystalline anisotropy may compete or sum up with shape anisotropy [8,9]. The change in pH of the electrolyte [10], the deposition rate, or aspect ratio [11], and the diameter [12] of Co nanowires result in different magnetic properties depending on phase structure and texture evolved.

Temperature dependent hysteresis behavior of magnetic nanowires is of great interest to understand the different anisotropy (shape, magnetocrystalline and magnetoelastic) contributions in deciding the magnetic properties. Different anisotropies and there specific temperature dependence have to be considered to explain such behaviors. Magnetocrystalline anisotropy increases more sharply with decrease of temperature whereas shape anisotropy does not show any significant change with temperature [13]. Additionally, often magnetoelastic anisotropy (K_{me}) originating from a different thermal expansion of nanowire, template and substrate is discussed [14–17].

There are a few reports showing strong temperature dependence of coercivity and remanence ratio in Co nanowires electrodeposited within alumina templates [18,19]. Recently, the temperature dependent magnetic properties of Co nanowires electrodeposited within track-etched polycarbonate membranes were discussed [20]. The temperature dependent remagnezation process in Co nanowires was attributed to magnetocrystalline anisotropy rather than magnetoelastic anisotropy.

In this paper, we report the temperature dependent hysteresis behavior and magnetic properties of Co nanowires electrode-

* Corresponding author. Present address: Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai 600036, India.
Tel.: +91 44 22575756; fax: +91 44 22570509.
E-mail address: ajeetshri@gmail.com (A.K. Srivastav).
[1] Present address: Centre for Solar Energy Technologies (CSET), Indian Institute of Technology Jodhpur, Jodhpur 342011, India.

0304-8853/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2013.08.041

posited within alumina templates with varying pH (3 and 6). There is a competition between shape and magnetocrystalline anisotropies in deciding the magnetic easy axis with change of temperature. The study rules out the contribution from magnetoelastic anisotropy in our system.

2. Experimental details

Porous anodic aluminum oxide template was prepared by a well established two-step anodizing process on aluminum foils [21]. Details of the template preparation have been reported in a previous paper [14]. Additionally, the remaining aluminum and the barrier layer were removed by chemical etching using $CuCl_2$ and H_3PO_4. The alumina templates show a homogenous well ordered hexagonal pore structure with 70 nm pore diameter and pore length variation between 15 and 20 μm. A thin Au layer was sputter-deposited on one side of the template to serve as a working electrode during electrodeposition. The mechanical stability of the membranes was enhanced by electrodepositing a few microns thick Cu layer onto backside of the Au layer.

Cobalt was deposited from 0.1 M $CoSO_4$ solution at room temperature for 30 min inside the alumina template using pH 3 and pH 6 solutions in a three-electrode cell. Boric acid (0.1 M H_3BO_3) was used as a buffer to maintain the pH in the vicinity of the electrode surface. The platinum foil was used as a counter electrode and saturated calomel electrode (SCE, 241 mV_{SHE}) as a reference electrode. The pH of as-prepared electrolyte was varied between 5 and 5.3 and the pH was maintained by using dilute NH_4OH and sulfuric acid. The depositions were carried out using an EG&G Potentiostat/Galvanostat Model 263A.

High resolution scanning electron microscopy (Leo 1530 Gemini) was used to examine the morphology at the cross-section of Co nanowires after breaking the template. The crystallographic analysis was done by X-ray diffraction (Phillips X′Pert PW 3400, Co Kα radiation). Magnetic measurements for both orientations (applied field parallel and perpendicular to the wire direction up to 3 T) were performed on Co nanowires embedded into the alumina template at varying temperatures (400–5 K) using a Vibrating Sample Magnetometer (Quantum Design Physical Property Measurement System).

3. Results

The alumina templates (Fig. 1) used had a very homogenous well ordered hexagonal pore structure with 70 nm and 100 nm pore diameter and pore-to-pore distance respectively. The Co nanowires of diameter 70 nm and 10 μm length (~150 aspect ratio) at pH 3 (Fig. 2a) and pH 6 (Fig. 2b) were electrodeposited within alumina templates. The depositions were carried out at potential of −1.0 V_{SCE}. The wire diameter and length of the wires were quite homogeneous and uniform throughout the deposition length.

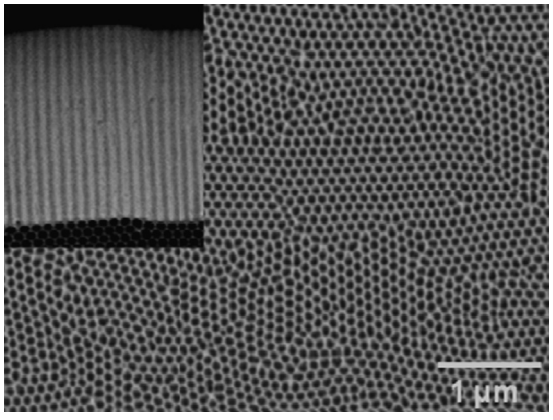

Fig. 1. HRSEM micrograph of an alumina template with ordered arrays of hexagonal nanopore structure (top surface and cross-sectional view).

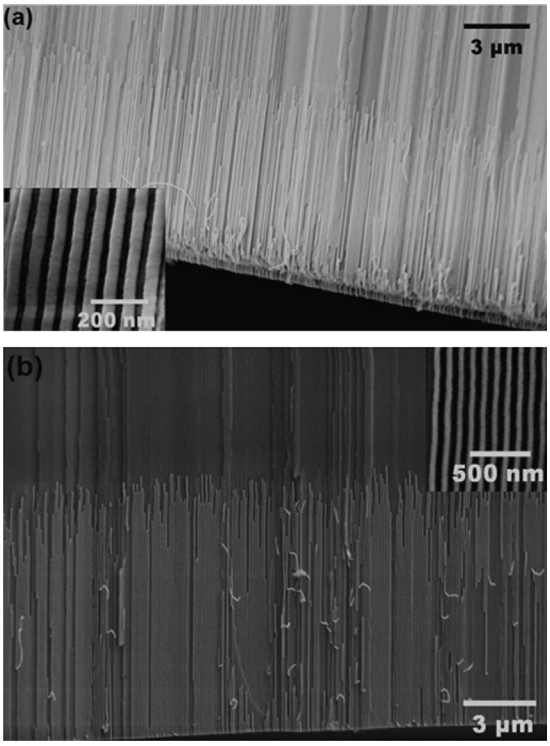

Fig. 2. HRSEM micrograph of Co nanowires electrodeposited at (a) pH 3 and (b) pH 6, showing uniformity of the wire growth throughout the length (inset shows the magnified view of the nanowires).

The effect of pH on phase structure evolution in electrodeposited Co nanowires was studied using XRD analysis (not shown) and has been discussed elsewhere [22]. The XRD analysis in combination with hysteresis behavior and magnetic properties showed that the fraction of *hcp* phase with the *c*-axis perpendicular to the wire axis was dominant in case of pH 3 and reduced significantly at pH 6.

The effect of pH on hysteresis behavior of Co nanowires embedded inside alumina templates has been illustrated in Fig. 3. The increase of pH from 3 to 6 favored effective anisotropy along the wire axis. The effect could be explained on the basis of phase structure evolving with increase of pH which favors less fraction of *hcp* phase with the *c*-axis orientated perpendicular to the wire axis. The crystal anisotropy competes with shape anisotropy in case of pH 3 and results in sheared hysteresis loop in comparison to pH 6 with field applied parallel to the wire axis (Fig. 3a). The loop becomes more squared in case of pH 3 in comparison to pH 6 with the field applied perpendicular to the wire axis (Fig. 3b). The coercivity and remanence ratio increased from 670 Oe and 0.18 to 840 Oe and 0.26 with increase of pH from 3 to 6 measured in the direction parallel to the wire axis, respectively. Likewise, coercivity and remanence ratio decreased from 460 Oe and 0.16 to 420 Oe and 0.09 with increase of pH from 3 to 6 measured in the direction perpendicular to the wire axis, respectively.

In order to study the effect of the *c*-axis orientation of *hcp* phase structure and the interplay between magnetic anisotropies (shape, magnetocrystalline and magnetoelastic), temperature dependent magnetic measurements were performed from 400 to 5 K. There was pronounced change in hysteresis behavior at low