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Orientation-controlled synthesis and magnetism of single crystalline Co nanowires

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ABSTRACT

Orientation control and the magnetic properties of single crystalline Co nanowires fabricated by electrodeposition have been systematically investigated. It is found that the orientation of Co nanowires can be effectively controlled by varying either the current density or the pore diameter of AAO templates. Lower current density or small diameter is favorable for forming the (1 0 0) texture, while higher current values or larger diameter leads to the emergence and enhancement of (1 1 0) texture of Co nanowires. The mechanism for the manipulated growth characterization is discussed in detail. The orientation of Co nanowires has a significant influence on the magnetic properties, resulting from the competition between the magneto-crystalline and shape anisotropy of Co nanowires. This work offers a simple method to manipulate the orientation and magnetic properties of nanowires for future applications.

1. Introduction

One-dimensional nanomaterials have attracted extensive interest due to their importance on fundamental research and functional properties [1–8]. The progress in synthetically tuning the physical properties of nanomaterials makes them exhibit enhanced optical, magnetic, mechanical and electronic properties in comparison with their bulk counterparts, that provide rich prospects for novel mechanical, biomedical, electronic and optoelectronic devices [2,7,9]. In particular, ferromagnetic nanowires represent a kind of system where intrinsic shape together with crystalline anisotropy can be exploited in a number of applications to spintronics [10], magnetic memory [11] and microwave devices [12]. Furthermore, the advancements in manufacturing of nanoelectronic devices have allowed the manufacturability of nanowire devices [9,13,14]. The performance of nanowire devices are found to greatly depend upon the crystallographic structures and their orientation of nanowires [14,15]. The growth control of nanowires is thus very essential for their future application.

Cobalt is a conventional and important ferromagnetic metal with large coercivity and high Curie temperature. The fabrication and behavior of Co nanowires have been motivated both by basic scientific interest in the magnetic properties and by their excellent application prospects for nanofunctional devices and sensors [1,12,16–20]. Among the various methods developed to prepare nanowires, electrodeposition combined with anodic aluminium oxide(AAO) template method is applied widely due to its convenience, inexpensiveness and large-scale processing [4,12,16]. It has been demonstrated that the magnetic properties of Co nanowires can be effectively modulated through varying the diameter [18,21,22]. However, the diameter variation of nanowires results in a change in the storage density or a rise in the interaction between neighboring nanowires, which will severely affect the performance of the potential devices [2]. It is more fascinating by modulating the orientation of nanowires since the magnetic property of bulk Co depends strongly on the crystalline orientations. So far, various strategies are adopted to control the orientation and magnetic property of Co nanowires by changing overpotential, bath temperature, pH of electrolytes, and the magnetic field applied during deposition [18,20–24]. For examples, Pirota et al. [16] reported that Co nanowires with two well-separated coexisting crystalline phases (fcc and hcp) can be controlled by the time of pulsed electrodeposition, thus their magnetic properties can be tuned according to the fcc/hcp length ratio. The effect of the electrolyte pH value on the crystal texture and the magnetic properties of Co nanowires were systematically studied by Ren et al. [18]. The direction of uniaxial magnetocrystalline easy axis in ac electrodeposited hcp Co nanowire arrays was found to depend strongly on the electrolyte temperature [22]. The magnetic field applied during deposition was also found to influence strongly the crystalline structure and magnetic

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properties Co nanowires [20]. Although much work has been done to control the orientation of Co nanowires, it is still a significant challenge to do it rationally.

Adjusting the electrodeposition current density and the pore diameter in this work, we focus on the manipulation of the orientation and magnetic properties of Co nanowires fabricated by electrodepositing Co^{2+} into AAO templates. The motivation for this choice (as opposed to the bath temperature, pH value, etc.) is that the current or diameter of pores can be accurately controlled as an external factor comparing to the solution parameters. The results reveal that the nanowires can be single-crystal with (1 0 0) or (1 1 0) orientation or polycrystalline by varying the current density or diameter, leading to diverse magnetic properties. This work offers a possible means to control the preferred orientation evolved and the magnetic properties of nanowires by simply varying the deposition parameters.

2. Experimental

Co nanowires were fabricated by DC electrodepositing Co^{2+} ions into AAO templates with the diameter of 55, 100 and 150 nm. All AAO templates were prepared with high-purity aluminum foil (99.999%) by a two-step anodizing process in a solution of 3 M oxalic acid at room temperature. To facilitate the electrodeposition, a gold layer of about 100 nm was sputtered on the back side of AAO template. A sulfate electrolyte with two fixed ingredient (0.178 M $CoSO_4 \cdot 7H_2O + 0.5$ M H_3BO_3) was used. The bath pH was adjusted to 3 by diluted H_2SO_4 solution. In the process of electrodeposition, the AAO templates were used as work electrode, and the graphite was used as auxilliary electrode. The DC electrodepositon was performed at constant current density of 2.6, 5.2 or 7.8 mA/cm^2.

The morphology of AAO and the prepared nanowires was observed by field emission scanning electron microscopy (SEM). The composition of the nanowires was analyzed by energy dispersive X-ray spectrometry (EDS). The structure of the nanowires embedded in AAO template was characterized using X-ray diffraction (XRD). A vibrating sample magnetometer was used to measure the magnetic properties of the samples at room temperature.

3. Results and discussion

The AAO template method is a general approach for preparing nanomaterials with almost uniform diameter. Fig. 1 displays the typical SEM images of AAO template and Co nanowires. The hexagonally ordered nanopores with monodisperse diameter of about 55 nm are observed (see Fig. 1(a)). The magnetic Co nanowires were grown by an electrodeposition process in the highly ordered AAO template. The cross section images of Co nanowires embedded in AAO template are shown in Fig. 1(b). It can be seen that Co nanowires are nearly 100%, homogeneously embedded in the highly ordered porous alumina matrix. The inset in Fig. 1(b) is the typical EDS spectrum of samples, suggesting that the nanowires are composed of Co and the labeled Al peaks are associated with aluminum coming from the AAO templates.

The current density can be accurately controlled during the DC electrodepositon. It is very interesting that only varying the current leads to different preferred-oriented nanowires with fixed diameter. Fig. 2(a)–(c) display the X-ray diffraction patterns of the Co nanowires fabricated at different current densities $i=2.6$, 5.2 and 7.8 mA/cm^2, respectively. One can see that at lower current density (i.e., 2.6 mA/cm^2), the Co nanowires are highly [1 0 0]-preferred-oriented single crystalline with the c axis

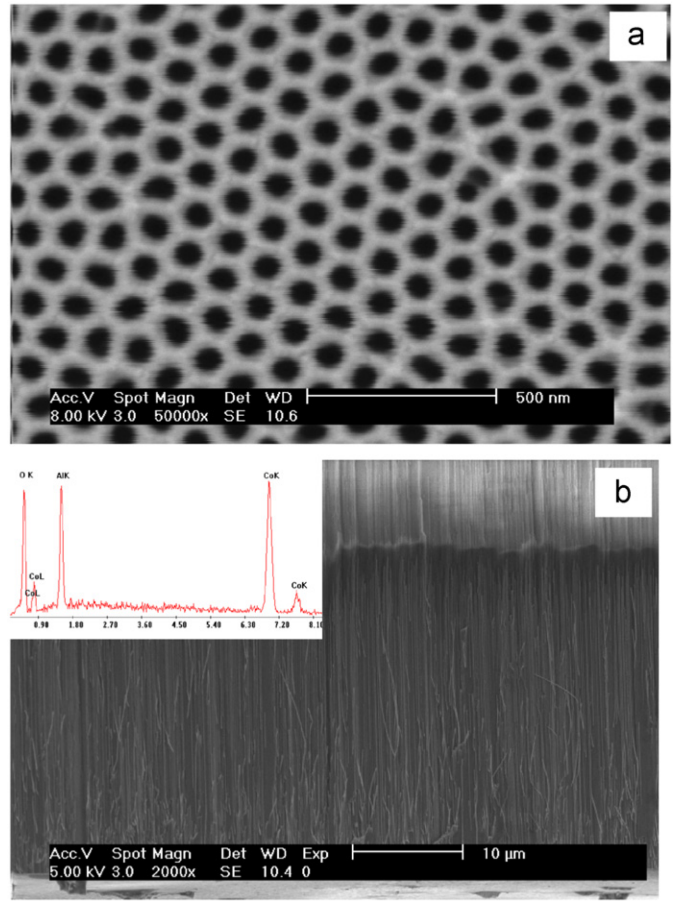

Fig. 1. Scanning electron microscopy images. (a) The top view of AAO template with an average pore size of 55 nm. (b) Cross section images of Co nanowire arrays. The inset shows the typic EDS.

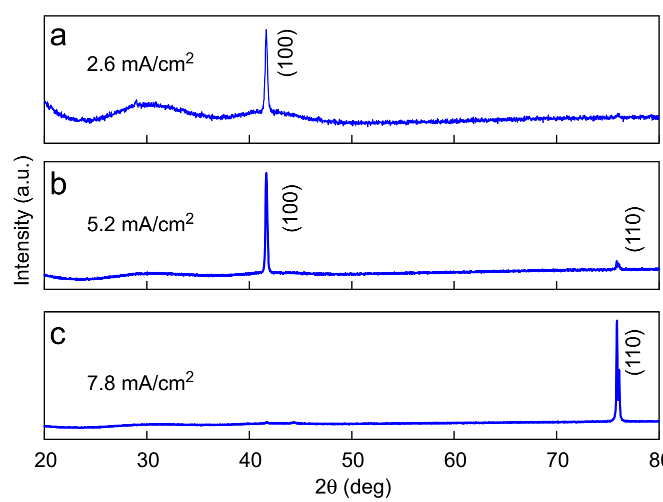

Fig. 2. XRD patterns of Co nanowire arrays fabricated with different current densities.

perpendicular to the long axis of the wire, which is confirmed by Fig. 2(a) where only one sharp and narrow peak from the (1 0 0) planes of hexagonal close-packed (hcp) Co(JCPDS No. 05-0727) can be observed. As the current density is increased to 5.2 mA/cm^2, the (1 1 0) plane of hcp Co emerges besides the (1 0 0) texture of the nanowires (see Fig. 2(b)). With further increasing the current density, the intensity of the (1 1 0) planes