Research Article

Diameter-Controllable Magnetic Properties of Co Nanowire Arrays by Pulsed Electrodeposition

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The Co nanowires with different diameters were prepared by pulsed electrodeposition into anodic alumina membranes oxide templates. The micrographs and crystal structures of nanowires were studied by FE-SEM, TEM, and XRD. Due to their cylindrical shape, the nanowires exhibit perpendicular anisotropy. The coercivity and loop squareness (M_r/M_s) of Co nanowires depend strongly on the diameter. Both coercivity and M_r/M_s decrease with increasing wire diameter. The behavior of the nanowires is explained briefly in terms of localized magnetization reversal.

1. Introduction

Magnetic nanowires have attracted much interest in the recent years for their potential applications in high-density magnetic recording devices. To realize these applications, the structure and the growth direction of nanowires need to be controlled precisely because the magnetic properties are related to these [1–3]. The synthesis and control of the magnetic nanostructure on a large scale is a challenging issue in the field of material science. One of the solutions is the method to combine electrodeposition with template [4]. Template-assisted electrodeposition is usually advantageous over other “dry” coating technologies due to its low cost, simple equipment, and large-scale processing [5]. Magnetic studies involving template synthesized ferromagnetic nanowire arrays are mainly focused on low-density arrays, even single ferromagnetic nanowire arrays of transition metals [6]. As for high density arrays, usually the magnetic behavior of very large aspect ratio wires is comparatively investigated between different metals [7, 8] and crystal structures [9, 10]. Therefore, more studies involving densely packed arrays are needed to understand the effect of aspect ratio, packing density on array magnetic properties, and to improve their potential in data storage applications.

As we know, cobalt is a hard magnetic material with tailorable magnetic properties through variation of the structural parameters. It was demonstrated in hcp Co nanowires that depending on texture, the shape and magnetocrystal anisotropies can either compete or add up to yield a partially controllable effective anisotropy [11, 12]. Highly ordered Co nanowire arrays with uniform diameter are essential for studying their properties and application in the high-density magnetic recording devices in future. Consequently, it has recently become a popular trend to try to control the crystal structure and magnetic properties of Co nanowire arrays by modifying the deposition parameters [13, 14]. In this study, the different diameters hcp Co nanowire arrays were fabricated by pulsed electrodeposition into anodic alumina membranes (AAMs). The magnetic properties of Co nanowires have also been investigated.

2. Experimental

The AAMs were prepared by a two-step anodization process [15, 16]. The barrier layer was dissolved in H_3PO_4 solution at 30°C for 30 minutes and the pore diameter of the as-prepared AAM is about 50 nm. While the AAM with pore size of 65 nm, 90 nm is obtained by etching in H_3PO_4 solution at 30°C for 40 minutes and 60 minutes, respectively.

FIGURE 1: FE-SEM images, TEM images, and XRD pattern of Co nanowires.

Finally a layer of Au film (about 200 nm) was sputtered onto one side of AAM to serve as the working electrode. The pulsed electrodeposition of the Co nanowire arrays was performed in a two-electrode electrochemical cell controlled by computer, and a graphite plate was used as the counter electrode. The typical electrolyte solution contains 0.2 M $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 40 g/L H_3BO_3 solution. The pH value of the electrolyte was adjusted to 5.0 by 1 M NaOH and the fabrication was performed at 27°C at the voltage of -3.0 V. The pulse frequency was 200 Hz ($T_{\text{on}} = 3.75$ ms, $T_{\text{off}} = 1.25$ ms).

The X-ray powder diffraction (XRD) pattern of the nanowire arrays was obtained by an X-ray diffractometer (D/MAX-rA) with Cu K α radiation ($\lambda = 1.54178$ Å). The morphologies were observed with field emission scanning electron microscope (FE-SEM) performed on JEOL JSM-6700F and a transmission electron microscope (TEM) on H-800. For the FE-SEM investigation, the sample was immersed in 3 wt% NaOH solution to partially remove the alumina template and then washed several times with deionized water.

The TEM specimen was obtained by completely dissolving the AAM in 5 wt% NaOH solution and then rinsed with absolute ethanol and immersed in an ultrasonic bath for 8 minutes. A Physical Property Measurement System (PPMS) was used to measure the hysteresis loops of the samples at room temperature.

3. Results and Discussion

The Microscopic morphology and XRD pattern of the Co nanowire arrays are shown in Figure 1. A large-area, high density, and high-order Co nanowires were liberated from the AAM and bundled together after partly dissolving the AAM can be seen. The nanowires are long and continuous, the surface is smooth, and diameter is uniform. The length of the nanowires is about 30 μm (Figure 1(a)), and the diameter is about 65 nm (Figures 1(b) and 1(c)). The aspect ratio (length/diameter) of the nanowires is about 460. The XRD pattern of as-prepared Co nanowire arrays is shown in Figure 1(d). All peaks can be indexed to the hcp phase, and

FIGURE 2: The magnetic hysteresis loops for different diameters Co nanowire arrays of 50 nm (a), 65 nm (b), and 90 nm (c).

match well with the standard diffraction peaks of Co (JCPDF 89-4308). The intensity for (10 $\bar{1}$ 0) planes is very strong and higher than others, which indicates that the nanowires have highly preferential orientation. The diffraction pattern which is corresponding to the area signed by the arrow can be indexed to hcp structure, and Co nanowires has a preferred orientation along the [10 $\bar{1}$ 0] direction (Figure 1(c)), which is in consistent with the result of the XRD.

Figure 2 shows the magnetic hysteresis loops for the Co nanowire arrays with different diameter, and the direction of the applied magnetic field is either parallel ($\theta = 0^\circ$, solid lines) or perpendicular ($\theta = 90^\circ$, dashed lines) to the axis of the nanowires. It is worth mentioning that bigger coercivity and loop squareness (M_r/M_s) (M_r is the remanent magnetization) indicate a strong magnetic anisotropy. It can be seen that, as the diameter increases, the H_c ($\theta = 0^\circ$)/ H_c ($\theta = 90^\circ$) values are 1424/584, 502/396, and 402/349 Oe; the M_r/M_s ($\theta = 0^\circ$) are 50%, 36.4%, 21.5%, while M_r/M_s ($\theta = 90^\circ$) are 20.3%, 15.7%, 9.8%. The results of the values of coercivity with the diameter of the nanowires illustrate that the shape anisotropy in the magnetization process plays an important role, and the easy axis along the wire (perpendicular to the film plane).

Nanowire magnetization process is generally in three areas by the following factors [17, 18]: magnetocrystalline anisotropy, shape anisotropy, and the interaction between the nanowires. Some works [19, 20] have reported that the effective anisotropy of the magnetic nanowire arrays comes from the competition between the magnetocrystalline anisotropy and the shape anisotropy. For hcp-phase Co, magnetocrystalline anisotropy energy density $K_1 = 5 \times 10^6$ erg/cm 3 is comparable to the shape anisotropy energy density $\pi M_s^2 = 6.0 \times 10^6$ erg/cm 3 [10], where M_s is the saturation magnetization of Co. Magnetocrystalline anisotropy of the hcp Co nanowires will make the magnetic moment arrange along the c -axis which perpendicular to the nanowire's axis in our experiments, but the shape anisotropy tends to arrange the magnetic moment along the axis of the nanowires [20]. So the competition between magnetocrystalline anisotropy and shape anisotropy results in a relatively weak effective anisotropy along the nanowire's axis, which leads to the low coactivity. When the diameter of the nanowires is small, each magnetic nanowire can be seen as a single domain magnetic structure. As the diameter increases, the single domain structure becomes multidomain. In the magnetization process, single domain structure of nanowires is through the atomic magnetic moment rotation to complete. The energy required to achieve this process than the energy of magnetic domain movement required is much greater. It makes small diameter nanowires with large coercivity. In contrast, the multidomain structure of nanowires is simply by moving magnetic domain to achieve in the magnetization process. This movement of energy consumed is small [21], so large diameter nanowire coercivity is smaller. The M_r/M_s changed by varying diameter is also this reason, when the external magnetic field becomes zero, the M_r/M_s decreases fast by the interaction of magnetic domains in the multidomain structure nanowires. That is the main reason that coercivity and M_r/M_s decrease

rapidly with increasing wire diameter from 50 nm to 65 nm.

Moreover, with increasing d , in-plane saturation field decreases (with perpendicular loop becoming more square) and out-of-plane saturation field dramatically rises (with parallel loop becoming more sheared). Contrary to square-like hysteresis loops of isolated (i.e., noninteracting) Co NWs [22] the parallel hysteresis loops are significantly sheared, hinting further on the presence of strong magnetostatic interactions between NWs. Even though the sample with the thickest wires ($d = 90$ nm) behaves similar to bulk-like ferromagnetic thin films, the out-of-plane (in-plane) coercivity still remains large (small). This can be attributed to the wire-like nature of the studied films. As the diameter increases from 65 nm to 90 nm, the coercivity and Mr/Ms decrease slowly. It should primarily be attributed to the evolution of magnetic interactions.

4. Conclusions

In summary, densely packed hcp Co nanowire arrays of varying diameter were obtained via pulsed electrodeposition into the pores of AAM. Dependence of magnetic properties on diameter, that is, aspect ratio, was investigated using PPMS at room temperature. It was observed that the magnetization easy axis lies parallel to Co nanowire axis. At the same time, the magnetic parameters, including coercivity, squareness, are highly correlated with diameter. So we can manipulate the magnetic property of Co nanowire arrays by changing the diameter of the nanowires.

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