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Structure and magnetic properties of Co nanowires in self-assembled arrays

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Abstract

Co nanowire arrays have been electrodeposited into self-assembled anodic aluminium oxide templates. It is found that the crystal structure of the Co nanowires depends on the pH value of the deposition electrolyte. The XRD results show that Co nanowires are fcc structure at $\text{pH} = 2.7$, a mixture of structures of fcc and hcp at $\text{pH} = 3.5$, and hcp structure at $\text{pH} = 5.0$. The effective anisotropy along the nanowire axis of the fcc Co nanowire array is obviously stronger than that of the hcp Co nanowire array, and the coercivity of the fcc structure is also larger than that of the hcp structure when they are the same diameter.

1. Introduction

A self-assembled template method such as the anodic aluminium oxide template (AAOT) has been employed to prepare nanowire arrays commercially [1–3]. A lot of magnetic nanowire arrays including Fe, Co, Ni and their alloys have been investigated [4–7]. The fabrication and properties of arrays of magnetic nanostructures are of interest not only from a fundamental, but also from a technological point of view. Their main fundamental interest lies in the emergence of novel magnetic and transport properties as the dimension approaches the length scale of a few nanometres to a few tens of nanometres. Technological interest lies in the potential application to future high density magnetic recording media, to electronic devices, and others.

The fabrication and magnetic properties of Co nanowire arrays have been published by many groups [8–14]. However, the relation between the experimental conditions and their crystal structures are disputed and not yet resolved. Kazadi and Ounadjela found that Co is stabilized in the hexagonal close-packed (hcp) structure with a preferential (002) texture oriented close to the perpendicular direction of the nanowire axis [11, 13]. However, Zeng and

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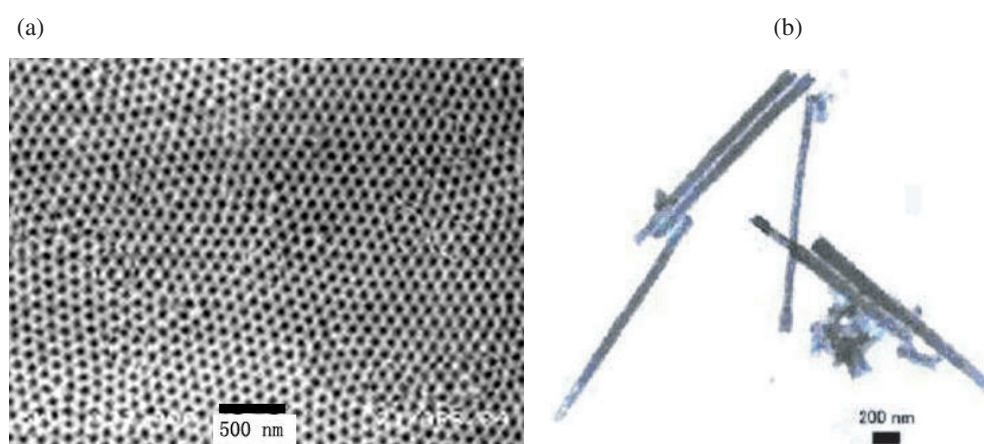


Figure 1. (a) SEM micrograph of AAO film with an average pore size of 70 nm, (b) TEM image of Co nanowires with diameter of 70 nm after removing the alumina.

Strijkers found Co nanowires consist of a mixture structures of face-centred cubic (fcc) and hcp [5, 6]. Paulus pointed out that Co nanowires can contain an amount of fcc phase which probably increases with decreasing nanowire diameter [10]. In this paper, we find that the crystal structure of Co nanowires depends strongly on the pH value of deposition electrolyte, and the magnetic properties of Co nanowire arrays also vary with their crystal structures.

2. Experiment

A 0.25 mm thick aluminium foil (99.999%) was used as starting material. To obtain highly ordered pores a two-step anodization process was employed. In the first anodization step, the Al was dc anodized for 15 min in acidic solution to form a layer of porous alumina. The alumina was then removed by a mixed solution of 0.2 M chromic acid and 0.4 M phosphoric acid at 60 °C. Subsequently, the sample was re-anodized for 1 h using the same parameters as in the first step. Finally, the voltage was reduced to 7 V. This led to a reduction of the barrier layer that formed between the porous alumina and the Al substrate, thus facilitating the electrodeposition of metals. The electrolyte consisted of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (120 g l^{-1}), boric acid (45 g l^{-1}). Its pH value was adjusted with NaHCO_3 solution. The deposition was done at different pH values (2.7, 3.5, and 5.0) by ac electrolysis at 15 °C, 200 Hz, 12 V_{AC} , and for 6 min.

Scanning electron microscopy (JSM-5600LV, Japan) and transmission electron microscopy (Philips EM-400T, Holland) was used to confirm the morphology of the AAO film and the Co nanowires. The crystal structure of the Co nanowire arrays was examined by x-ray diffraction (Philips x'pert, Holland). A vibrating sample magnetometer (Lakeshore 730, USA) was used to measure the magnetic properties of the samples at room temperature.

3. Results and discussion

Figure 1(a) shows a SEM micrograph of an AAO film with average pore size of 70 nm. One can see that the distribution of pores is almost uniform. Co was electrodeposited into the pores of anodic aluminium oxide, and figure 1(b) shows a TEM image of Co nanowires with diameter of 70 nm after removing alumina. The aspect ratio of the nanowires is greater than

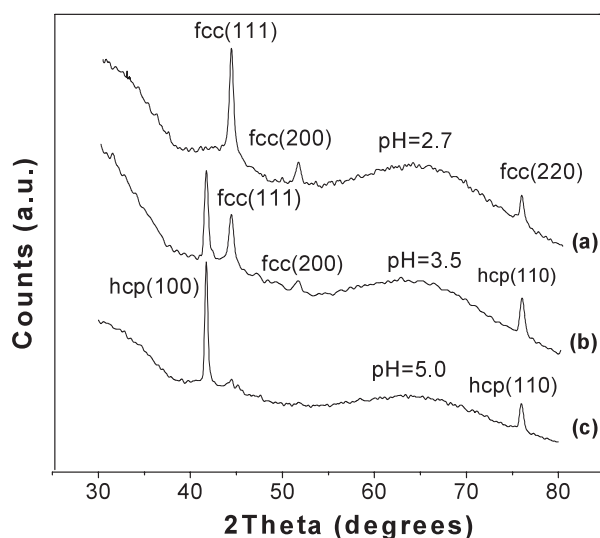


Figure 2. X-ray diffraction patterns of Co nanowire arrays deposited at (a) pH = 2.7, (b) pH = 3.5 and (c) pH = 5.0.

20. Typical x-ray diffraction patterns of Co nanowire arrays embedded within the AAO film deposited (a) at pH = 2.7, (b) at pH = 3.5, and (c) at pH = 5.0 are shown in figure 2. The θ - 2θ scan was performed with the scattering vector perpendicular to the nanowire axes (parallel to the plane of AAO). Significant differences of crystal structures are observed from the three patterns, indicating the crystal structure of Co nanowires depends strongly on the pH value of electrolyte. When pH = 2.7, the diffraction pattern of Co is shown in figure 2(a). The strongest peak of the diffraction pattern appears at 44.212° . It accords with the peak of the (111) plane of standard fcc Co which appears at 44.216° , although it is similar to the peak of the (002) plane of hcp Co which appears at 44.599° . In addition, there is a special (200) peak of fcc Co which can distinguish from hcp Co at the position of 51.522° . This peak also appears in our result (figure 2(a)). So, Co is crystallized in the fcc structure (figure 2(a)) when pH = 2.7. As the pH value of electrolyte is maintained at 3.5 (figure 2(b)), the peak of the (100) plane of the hcp structure appears in addition to that of the (111) plane of the fcc structure, and the Co nanowires are crystallized in a mixture structure of fcc and hcp. This structure is consistent with the published results of Zeng and Strijkers [5, 6]. However, when the pH value of electrolyte is changed to 5.0 (figure 2(c)), the peaks of the fcc structure almost disappear, and Co is crystallized in the hcp structure. From this pattern, we can see the peaks of the (002) and (101) planes of the hcp structure disappear. Comparing this result to that of standard powder diffraction of hcp Co, the relative intensity of the three peaks is 38:63:100. So, it is reasonable to accept that the hexagonal *c* axis lies preferentially perpendicular to the long axis of nanowire [11, 13]. The experimental results of figure 2 demonstrate the strong influence of the pH value on the structure of Co nanowires during their deposition. The crystal structure of Co nanowires is fcc when the pH value of the electrolyte is 2.7, but transform to hcp as the pH value is changed to 5.0. The following are the magnetic properties of Co nanowire arrays of different crystal structures.

Figure 3 illustrates the typical angular dependence of the coercivity and squareness for Co nanowire arrays of fcc and hcp structures, where θ is the angle between the nanowire axis and the applied field during measurement. It can be observed that the maximum coercivity and squareness occur when the applied field is parallel to the nanowire axis for the two samples of

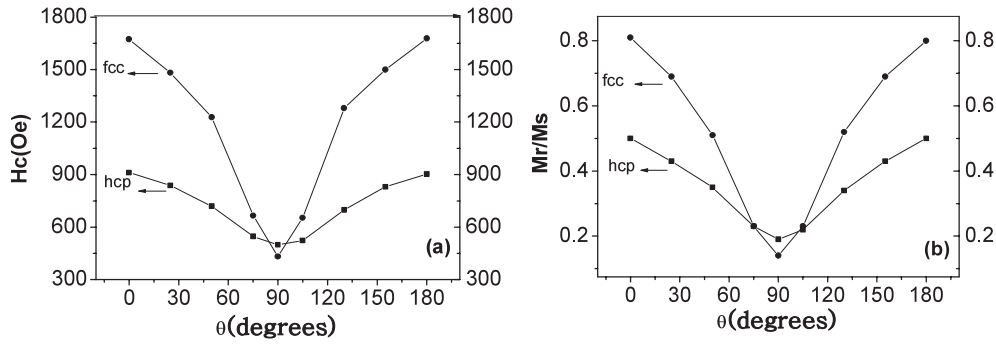


Figure 3. The angular dependence of (a) coercivity and (b) squareness for fcc and hcp Co nanowire arrays with a diameter of 70 nm.

Table 1. Effective anisotropy of different crystal structure Co nanowire arrays with diameters of 15 and 70 nm.

d_w (nm)	K_{eff} (fcc) (10^6 erg cm^{-3})	K_{eff} (hcp) (10^6 erg cm^{-3})
15	3.31	2.40
70	3.10	1.30

different structures, indicating that their easy axes are all along the nanowire, and the shape anisotropy is predominant for the two samples. But the coercivity and squareness of the fcc Co nanowire array are larger than those of the hcp Co nanowire array at the same θ except $\theta = 90^\circ$.

Figure 4 shows the magnetization curves for $d_w = 15$ and 70 nm Co nanowire arrays of (a), (b) hcp and (c), (d) fcc structures with the applied field parallel and perpendicular to the nanowire axis, respectively. The maximum value of the applied field is 1.2 T. When a magnetic sample is magnetized to saturation, the area between the magnetization curve and the magnetic moment denotes the work (W) of the external field. Here, the effective anisotropy constant (K_{eff}) of the Co nanowire array is denoted as

$$K_{\text{eff}} = \frac{1}{v}(W_{\perp} - W_{\parallel}), \quad (1)$$

that is the area between the magnetization curves with field orientation parallel (\parallel) and perpendicular (\perp) to the nanowire axes. If spontaneous magnetization (M_s) is introduced, equation (1) may be expressed as

$$K_{\text{eff}} = \frac{M_s}{m_{\text{tot}}} \int_0^{m_{\text{tot}}} H_{\perp} dm - \frac{M_s}{m_{\text{tot}}} \int_0^{m_{\text{tot}}} H_{\parallel} dm, \quad (2)$$

where m_{tot} is the magnetic moment of the sample which is magnetized to saturation and H_{\parallel} , H_{\perp} is the external field along the nanowire axis and perpendicular to the nanowire axis, assuming the spontaneous magnetization of Co nanowires is equal to the bulk value [14]. Experimental results are shown in table 1. The effective anisotropy constants (K_{eff}) of the fcc structure are larger than those of the hcp structure when the nanowires are in the same diameter. This indicates that Co nanowire arrays of different crystal structures exhibit different effective anisotropy and the effective anisotropy of fcc is stronger than that of the hcp structure.

Figure 5 depicts the typical magnetic hysteresis loops for 15 and 70 nm Co nanowire arrays of (a), (c) fcc and (b), (d) hcp structures. The hysteresis loops were measured with

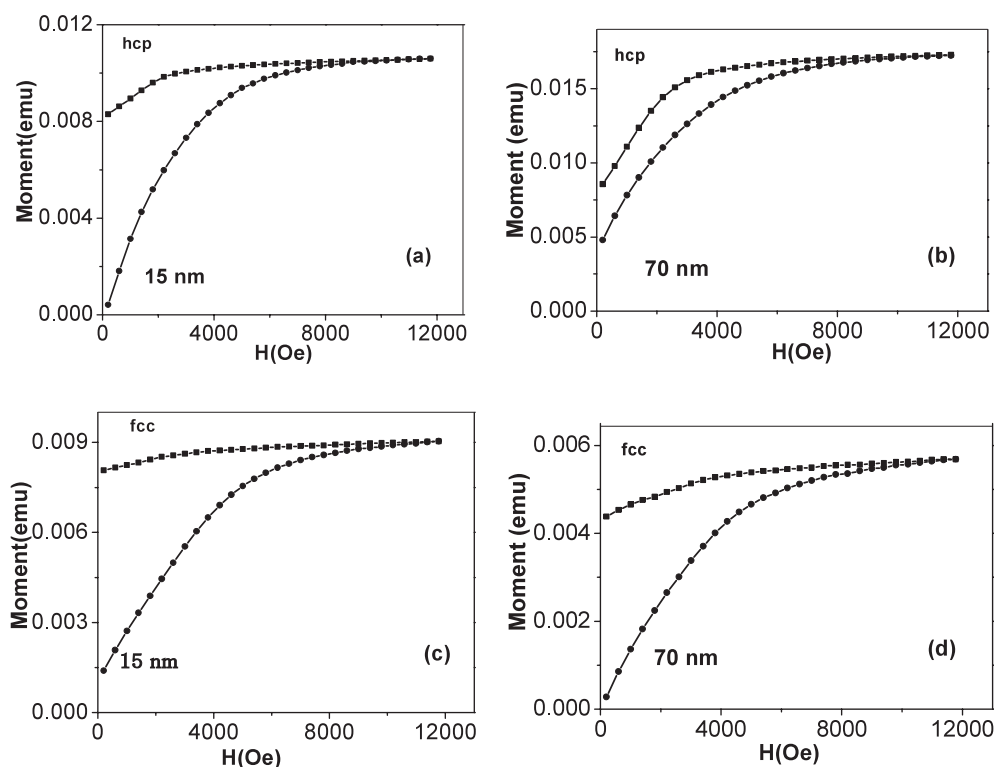


Figure 4. Magnetization curves at room temperature of the Co nanowire arrays with diameters of 15 nm (a), (c) and 70 nm (b), (d) for different crystal structure, with the applied field parallel (-■-) and perpendicular (-●-) to the nanowire axis.

the applied magnetic field parallel and perpendicular to the nanowire axis, respectively, at room temperature. The four samples all exhibit uniaxial anisotropy, with the easy axes along the nanowire axis. When magnetic field is parallel to the nanowire axis, the coercivity and squareness of the Co nanowire arrays of fcc structure are much larger than those of the hcp structure when they are in the same diameter.

The different magnetic properties of Co nanowire arrays of different crystal structures are due to the difference in magnitude of the magnetocrystalline anisotropy. For an infinite cylinder, the shape anisotropy tends to align the magnetic moment along the axis of the cylinder. When the magnetocrystalline anisotropy can be ignored in comparison with the shape anisotropy, the effective anisotropy of the nanowire arrays is mostly determined by the shape anisotropy, resulting in large coercivity and squareness along the nanowire axis, which is also obtained for bcc Fe and fcc Ni nanowires with small diameter [15, 16]. While the magnetocrystalline anisotropy is comparable to the shape anisotropy, the effective anisotropy of the nanowire is determined by both of them. In the case of hcp Co, its magnetocrystalline anisotropy energy density (of the order of $K_1 = 5 \times 10^6 \text{ erg cm}^{-3}$) is comparable to the shape anisotropy energy density ($\pi M_s^2 = 6 \times 10^6 \text{ erg cm}^{-3}$) [14]. According to the results of the XRD (figure 2(c)), the hexagonal c axis of Co nanowires crystallized in hcp structure lies preferentially perpendicular to the long axis of nanowire. Magnetocrystalline anisotropy of hcp structure Co nanowires tends to align the magnetic moment perpendicular to the wires. Thus, the competition between magnetocrystalline anisotropy and shape anisotropy results in

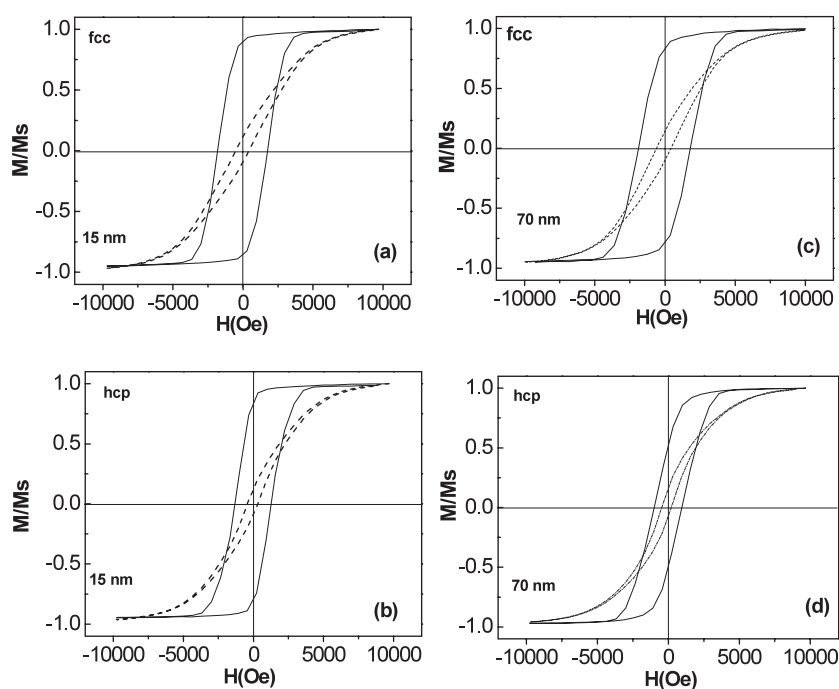


Figure 5. Magnetic hysteresis loops at room temperature of the Co nanowire arrays with diameters of 15 nm (a), (b) and 70 nm (c), (d) for different crystal structure, with the applied field parallel (solid curves) and perpendicular (dashed curves) to the nanowire axis.

a weaker effective anisotropy along the nanowire axis, which leads to the lower coercivity and squareness (figures 3 and 5(b), (d)) of the nanowire array. At room temperature, fcc and hcp Co have the same saturation magnetization ($M_S(\text{hcp}) = M_S(\text{fcc})$) [17]. So, they have the same shape anisotropy energy density. For fcc Co, the magnetocrystalline anisotropy energy density ($K_1 = 6.3 \times 10^5 \text{ erg cm}^{-3}$) can be ignored in comparison with the shape anisotropy energy density ($K_1 = 6 \times 10^6 \text{ erg cm}^{-3}$). The effective anisotropy of the fcc Co nanowires is mostly determined by shape anisotropy. As a result, the Co nanowire array of fcc structure exhibits larger coercivity and squareness (figures 3 and 5(a), (c)) than those of hcp structure along the nanowire axis, indicating a more remarkable perpendicular magnetic anisotropy.

H_c as a function of diameter (d_w) for Co nanowire arrays of fcc and hcp structures is shown in figure 6. All samples of fcc and hcp structures were deposited as the pH values of electrolyte were 2.7 and 5.0. H_c of the fcc structure is larger than that of the hcp structure for all diameters. When the diameter is 15 nm, the gap of coercivity between the fcc and hcp structure Co nanowire arrays is about 490 Oe, but increases to about 690 Oe when the diameter increases to 70 nm. This can be understood by the obvious decrease of effective anisotropy constant with diameter increase for the hcp Co nanowire array. The effective anisotropy constant for the 15 nm Co nanowire array of the hcp structure is $2.40 \times 10^6 \text{ erg cm}^{-3}$. As the diameter increases to 70 nm, it decreases by 46% (table 1). The obvious decrease of the effective anisotropy constant results in a lower coercivity with increasing nanowire diameter, indicating that the coercivity of the Co nanowire array is dependent on its effective anisotropy constant, and their quantitative relation is still an open question. The reason why the effective anisotropy constant decreases obviously with diameter increase for hcp Co nanowire arrays may be that

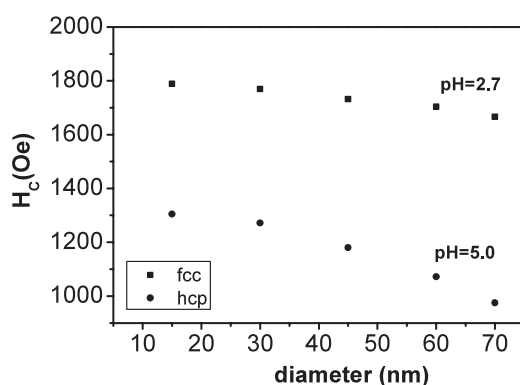


Figure 6. Coercivity as a function of nanowire diameter for fcc (deposited at pH = 2.7) and hcp (deposited at pH = 5.0) Co nanowire arrays when the external field is applied parallel to the axis of the nanowire at room temperature.

the hexagonal c axis is more preferentially perpendicular to the long axis of the nanowire with the diameter increase. In addition, the results of the effective anisotropy constant are also associated with the following reasons: (i) polycrystallinity, crystalline defects and impurities exist in nanowires, (ii) the c axis of hcp is not strictly perpendicular to the long axis of the nanowires, (iii) dipole interaction exists in the nanowire array.

4. Conclusions

In summary, the crystal structure of the Co nanowires is strongly dependent on the pH value of the electrolyte. It is fcc structure when the value of electrolyte is 2.7, and changes to hcp as the pH value of electrolyte is 5.0. Magnetic measurements show the easy axes are all along the nanowire axis for Co nanowire arrays of different crystal structures, but the effective anisotropy constant of the fcc structure is obviously stronger than that of the hcp structure, and the coercivity of the fcc structure is also larger than that of the hcp structure when they are the same diameter. This is explained considering the competition between shape anisotropy and magnetocrystalline anisotropy for the hcp Co nanowires, and the effective anisotropy of fcc Co nanowires is determined mostly by shape anisotropy.

Acknowledgment

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