

Magnetic properties of single crystalline Co nanowire arrays with different diameters and orientations

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Single crystalline Co nanowire arrays with different diameters and orientations were grown within porous anodic alumina membranes by a pulsed electrodeposition technique and the magnetic properties of the nanowire were systematically studied. It was found that the magnetization behavior of the Co nanowire arrays is anisotropic and their magnetic properties can be effectively modulated through tuning either the diameter or the orientation of the nanowires. The magnetic properties of the Co nanowires were discussed qualitatively by using the classical magnetization theory and single domain model. © 2009 American Institute of Physics. [DOI: 10.1063/1.3108529]

I. INTRODUCTION

Magnetic nanowire arrays have attracted much interest recently due to their great promise for magnetic memory and spintronics applications.^{1–3} Cobalt is an important ferromagnetic material with large coercivity and high Curie temperature. The fabrication of Co nanowire arrays has been the focus of many studies.^{4–6} In practical applications, the tunable magnetic property is essential, which has been obtained by several strategies. One is changing the diameter of the nanowires,⁷ but the expense is either 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.⁸ The other is incorporating nonmagnetic elements in the magnetic nanowires,^{9,10} and as a result the nonmagnetic elements will affect the mechanical and thermal stability of the nanowires. In fact, the most fascinating strategy is modulating the orientation of nanowires, as we all know that the magnetic property of bulk Co differs greatly along the different crystalline orientations.¹¹

Up to now, the study on the orientation dependence of magnetic properties for Co nanowire arrays is scarce mainly due to the difficulty in the fabrication of Co nanowire arrays with tunable orientations. Recently, we have successfully fabricated single crystalline Co nanowires with well-controlled orientations through pulsed electrodeposition in anodic alumina membranes (AAMs).¹² In this paper, we report the dependence of magnetic properties of Co nanowire arrays on the diameter and orientation in detail and an anisotropic magnetization behavior is demonstrated.

II. EXPERIMENTAL

The AAM was prepared by a two-step anodization process as described in previous reports.^{13–17} The electrolyte was comprised of 0.1 M CoSO₄·7H₂O and 0.5 M H₃BO₃. Pulsed electrodeposition was carried out under modulated

voltages control through a computer. The detailed preparation condition of Co nanowire arrays can be found elsewhere.¹²

The crystal structure and morphology of nanowire arrays were characterized by x-ray diffraction (XRD) using Cu K α ($\lambda=1.542$ Å) radiation, field emission scanning electron microscopy (FESEM) (FEI Sirion 200), and transmission electron microscopy (TEM) (JEM-2010) attached with selected area electron diffraction (SAED). For FESEM observation, the AAM was partially etched in 5% NaOH solution and then washed with distilled water for several times. For TEM observations, the AAM was completely dissolved in a 5% NaOH solution and then washed with distilled water several times and finally dispersed in absolute ethanol by ultrasonic. The magnetic properties of nanowires with the membrane support were investigated on a Quantum Design superconducting quantum interference device magnetometer at 300 K.

III. RESULTS AND DISCUSSION

A. Characterization of the nanowires

Figure 1 shows the FESEM images of Co nanowires with different diameters after etching the AAM partially. Apparently, the Co nanowires are large area, high filling and highly ordered, and replicate the pore arrangement of AAM. The corresponding diameter of the nanowires is about 40, 70, and 110 nm with an average length of about 40 μ m and the

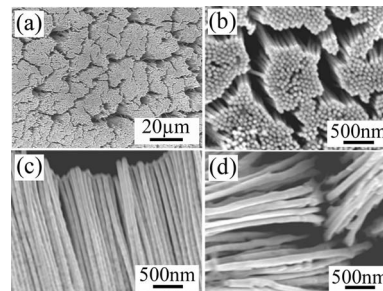


FIG. 1. FESEM images of Co nanowire arrays with the diameter of (a) and (b) 40, (c) 70, and (d) 110 nm.

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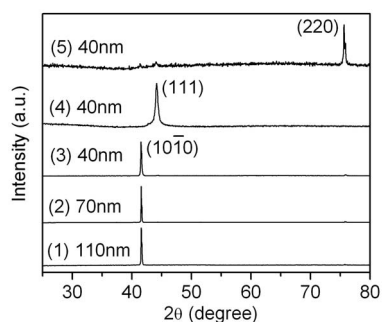


FIG. 2. XRD patterns of Co nanowire arrays with different diameters and orientations.

aspect ratio (length/diameter) over 360, which is beneficial to prevent the onset of superparamagnetism in magnetic data storage.¹

XRD patterns of Co nanowire arrays with different diameters and growth orientations are shown in Fig. 2. The diffraction peaks for curves (1)–(3) can be indexed to hcp Co (Ref. 18) while those for curves (4) and (5) can be indexed to fcc Co (Ref. 19). The sharp and narrow peaks at about 41.6° , 44.3° , and 75.9° are extremely strong compared to other peaks, indicating the highly preferential orientation of the corresponding nanowires along $[10\bar{1}0]$, $[111]$, and $[220]$ directions, respectively. These results have been confirmed by TEM analysis in the following text.

Figures 3(a)–3(d) show the TEM images of the Co nanowires with same orientation but different diameters and the corresponding SAED patterns (the insets) show that these nanowires are all single crystalline with the growth orientation along hcp $[10\bar{1}0]$ direction. The array feature and even the Au electrode layer on the end of the nanowires can still be seen after releasing of the nanowires from the AAM, as shown in Fig. 3(c). Figures 3(e) and 3(f) show the TEM images of one individual Co nanowire with the same diameter of about 40 nm but different orientations and the corresponding SAED patterns can be well indexed to fcc Co with

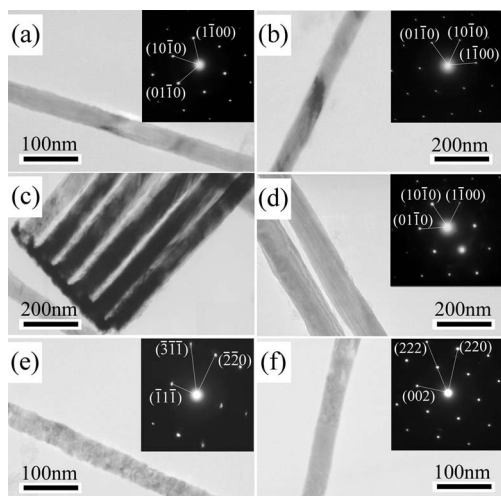


FIG. 3. TEM images and the corresponding SAED patterns of Co nanowires with the orientation of hcp $[10\bar{1}0]$ and diameter of (a) 40, (b) 70, (c) 70, and (d) 110 nm and with the diameter of 40 nm and orientation of (e) fcc $[111]$ and (f) fcc $[220]$.

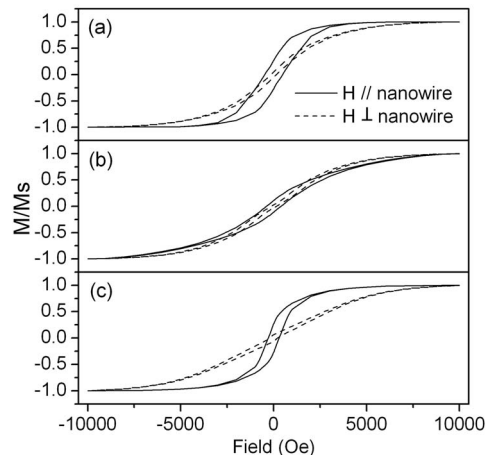


FIG. 4. Magnetic hysteresis loops of Co nanowire arrays with the diameter of (a) 40, (b) 70, and (c) 110 nm.

orientation along $[111]$ and $[220]$, respectively. The TEM analyses are well consistent with the XRD results. More detailed characterization and growth mechanism can be found elsewhere.¹²

B. Diameter- and orientation-dependent magnetic properties

Figure 4 shows the magnetic hysteresis loops of Co nanowire arrays with the same orientation ($[10\bar{1}0]$) but different diameters. Corresponding coercivity and squareness values are listed in Table I. One can see that the coercivity decreases from about 476 to 282 Oe with increase in the diameter from 40 to 110 nm on the direction of parallel to the nanowires, indicating that the switching is expected to occur by curling.²⁰ For the nanowire array with the diameter of 40 and 70 nm the coercivity and the squareness decrease gradually no matter the magnetic field is parallel or perpendicular to the axis of nanowires, which is attributed to an increase in the magnetostatic interaction field with decreasing the distance between the nanowires.^{21,22} The interaction between the neighboring nanowires is expected to intensify when the nanowires in the array are close to each other, which will induce a crosstalk between neighboring nanowires and affect the performance of the magnetic storage devices.⁸ From this perspective, changing the diameter to adjust the magnetic properties of nanowires is not a good route when used as magnetic storage medium.

The orientation modulation provides a new opportunity to manipulate the magnetic property of Co nanowire arrays without changing the diameter and the composition. Figure 5 shows the magnetic hysteresis loops of the Co nanowire ar-

TABLE I. Coercivity and squareness of Co nanowire arrays with different diameters.

		40 nm	70 nm	110 nm
Squareness		0.272	0.111	0.226
	⊥	0.047	0.025	0.061
Coercivity (Oe)		476.9	390.4	292.7
	⊥	139.2	127.9	201.0

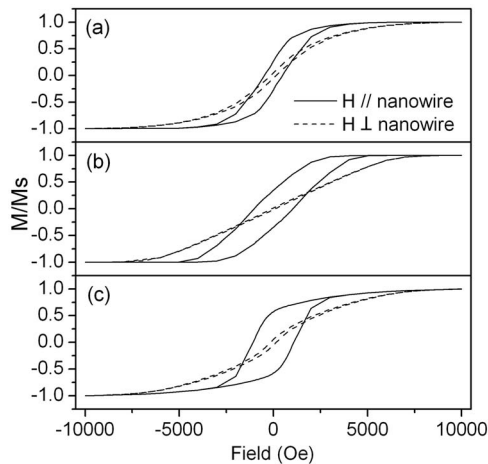


FIG. 5. Magnetic hysteresis loops of Co nanowire arrays with the orientation of (a) hcp $[10\bar{1}0]$, (b) fcc $[220]$, and (c) fcc $[111]$.

rays with the same diameter but different orientations. The preferential orientation of the nanowires is along $[10\bar{1}0]$, $[220]$, and $[111]$, respectively. It can be seen that the nanowires are more easily magnetized along the direction parallel than perpendicular to nanowires due to the large shape anisotropy (SA).²³ The loops have a sheared rectangular shape when the applied field is parallel to the nanowire axis, while those have a more sheared shape when the applied field is perpendicular to the wire axis, illustrating a strong magnetic anisotropy. The dependences of the coercivity and squareness on the orientation of the nanowires are shown in Table II. One can see that the coercivity parallel to the nanowires gradually increases with the orientation of the nanowires turns from hcp $[10\bar{1}0]$ to fcc $[220]$ and to fcc $[111]$.

The above results demonstrated that the magnetic properties of the Co nanowire arrays can be modulated independently via either adjusting the diameter or tuning the orientation of the nanowire. Apparently, the magnetic properties of the nanowires can be modulated to larger extent through combining these two factors. Such an example is shown in Fig. 6, which shows the hysteresis loops of Co nanowire arrays with the orientation along fcc $[111]$ and diameter of about 25 nm. Strong magnetic anisotropy can be seen and the coercivities parallel and perpendicular to nanowire axis are 1614 and 300 Oe, respectively. This result further demonstrates the possibility of designing the nanowire array to meet the demands of practical devices.

C. Discussion

It is well known that ultrafine ferromagnetic particles exhibit a greatly enhanced magnetic coercivity with two or-

TABLE II. Coercivity and squareness of Co nanowire arrays with different orientations.

		$[10\bar{1}0]$	$[220]$	$[111]$
Squareness	\parallel	0.272	0.345	0.574
	\perp	0.047	0.012	0.053
Coercivity (Oe)	\parallel	476.9	1031	1075
	\perp	139.2	86.4	149.2

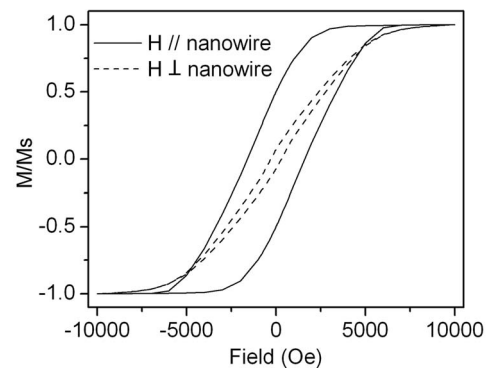


FIG. 6. Magnetic hysteresis loops of Co nanowire arrays with a diameter of 25 nm and fcc $[111]$ orientation.

ders of magnitude higher than the bulk material due to the single-domain nature of the particles. Compared with the coercivity value of bulk cobalt (a few tens of oersteds),²⁴ an obvious increase for Co nanowires was observed in the present study, which are attributed to the anisotropic morphology and the highly preferential orientation of the Co nanowires.²⁵

From Figs. 5(a)–5(c), one can see that both the solid and dashed lines will join together at about 7500 Oe, indicating that the magnetic anisotropies for these three nanowire arrays are roughly the same. This magnetic anisotropic field is much larger than that of the coercive field along the nanowires. Previous studies suggested that the critical radius of a single-domain sphere in a nanowire is much larger than that of an isolated single-domain sphere.^{26–28} So in the following discussion a single domain model was used for simplification due to the fact that the diameter of the single crystalline Co nanowire is close to the critical radius of spherical Co single domain.

Generally, the anisotropy magnetization originates from the competitive contributions of both magnetocrystalline anisotropy (MA) and SA. Here the aspect ratio of the nanowire exceeds 360 and if the nanowire is considered as an infinite cylinder, then the SA tends to align the magnetization along the axis of the nanowire. For the case of Co nanowires grown along hcp $[10\bar{1}0]$, the magnetocrystalline easy axis is along $[0001]$, which is perpendicular to the axis of the nanowire.⁶ Thus there is a direct competition between MA and SA. The SA energy density ($\pi \times M_s^2 \sim 6 \times 10^6$ erg cm⁻³) is slightly larger than the MA energy density ($K_1 \sim 5 \times 10^6$ erg cm⁻³). The competition will result in a reduced coercivity and squareness in the hcp Co nanowire arrays. For the Co nanowires with a fcc structure, the SA has the same value as the one in the hcp structure because of the same saturation magnetization [$M_s(\text{fcc}) = M_s(\text{hcp})$] at room temperature.²⁹ The magnetocrystalline easy axis is along $[111]$ direction³⁰ and the MA energy density [$K_1 \sim 6.3 \times 10^5$ erg cm⁻³] is almost one order of magnitude smaller than that of SA energy density, and there is an angle of about 35.26° between the magnetocrystalline easy axis and the axis of the nanowire for Co nanowire grown along $[220]$. The MA energy only partially contributes to the coercivity along the nanowires. For Co nanowire grown along $[111]$, both MA and SA act coopera-

tively along the axes of the nanowires³⁰ and the MA energy will totally contribute to the coercivity along the nanowires. Consequently, the coercivity of the fcc [111] is slightly larger than that of fcc [220] Co nanowire arrays, both of which are much larger than that of hcp [10 $\bar{1}$ 0] Co nanowire arrays, as demonstrated in Fig. 5.

It is worthy to note that the squareness along the nanowire is not very high due to several factors. First, the nanopores of the AAM are not perfectly aligned perpendicular to the template plane.³¹ Second, the most easily magnetization directions are not all along the nanowire. Third, the nanowires are too long to guarantee that only one magnetic domain exists in an individual nanowire, i.e., the nanowire may consist of multidomains. All these factors will lead to a small squareness and the last one is thought to play the dominant role in the present study.

IV. CONCLUSIONS

Single crystalline Co nanowire arrays with different orientations and diameters were synthesized and their magnetic properties were studied. It is found that the magnetization behavior is similar for Co nanowire arrays with different diameters but the same orientation, while that is anisotropic with different orientations. Due to the interaction between MA and SA, the magnetic properties of the Co nanowires can be modulated more effectively through tuning orientation than diameter, which is very important in controlling the magnetic properties of nanowires to meet the different needs in future applications.

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¹T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, and T. P. Russell, *Science* **290**, 2126 (2000).

²R. Skomski, *J. Phys.: Condens. Matter* **15**, R841 (2003).

³K. R. Pirota, E. L. Silva, D. Zanchet, D. Navas, M. Vázquez, M. Hernández-Vélez, and M. Knobel, *Phys. Rev. B* **76**, 233410 (2007).

⁴S. A. Gusev, N. A. Korotkova, D. B. Rozenstein, and A. A. Fraerman, *J. Appl. Phys.* **76**, 6671 (1994).

⁵A. Ursache, J. T. Goldbach, T. P. Russell, and M. T. Tuominen, *J. Appl. Phys.* **97**, 10J322 (2005).

⁶J. Zhang, G. A. Jones, T. H. Shen, S. E. Donnelly, and G. H. Li, *J. Appl. Phys.* **101**, 054310 (2007).

⁷D. J. Sellmyer, M. Zheng, and R. Skomski, *J. Phys.: Condens. Matter* **13**, R433 (2001).

⁸Z. K. Wang, H. S. Lim, V. L. Wang, J. L. Goh, S. C. Ng, M. H. Kuok, H. L. Su, and S. L. Tang, *Nano Lett.* **6**, 1083 (2006).

⁹Y. W. Wang, L. D. Zhang, G. W. Meng, X. S. Peng, Y. X. Jin, and J. Zhang, *J. Phys. Chem. B* **106**, 2502 (2002).

¹⁰J. Choi, S. J. Oh, H. Ju, and J. Cheon, *Nano Lett.* **5**, 2179 (2005).

¹¹W. D. Zhong, *Ferromagnetism* (Scientific, Princeton, NJ, 1998).

¹²X. H. Huang, L. Li, X. Luo, X. G. Zhu, and G. H. Li, *J. Phys. Chem. C* **112**, 1468 (2008).

¹³Y. Zhang, G. H. Li, Y. C. Wu, B. Zhang, W. H. Song, and L. D. Zhang, *Adv. Mater. (Weinheim, Ger.)* **14**, 1227 (2002).

¹⁴L. Li, Y. W. Yang, X. H. Huang, G. H. Li, and L. D. Zhang, *Nanotechnology* **17**, 1706 (2006).

¹⁵C. H. Liang, K. Terabe, T. Hasegawa, and M. Aono, *Nanotechnology* **18**, 485202 (2007).

¹⁶X. C. Dou, G. H. Li, and H. C. Lei, *Nano Lett.* **8**, 1286 (2008).

¹⁷G. Kartopu, O. Yalçın, M. Es-Souni, and A. C. Başaran, *J. Appl. Phys.* **103**, 093915 (2008).

¹⁸JCPDS Card No. 89-4308.

¹⁹JCPDS Card No. 89-307.

²⁰J. Mallet, K. Y. Zhang, C. L. Chien, T. S. Eagleton, and P. C. Searson, *Appl. Phys. Lett.* **84**, 3900 (2004).

²¹H. Zeng, M. Zheng, R. Skomski, D. J. Sellmyer, Y. Liu, L. Menon, and S. Bandyopadhyay, *J. Appl. Phys.* **87**, 4718 (2000).

²²J. C. Bao, C. Y. Tie, Z. Xu, Z. Y. Suo, Q. F. Zhou, and J. M. Hong, *Adv. Mater. (Weinheim, Ger.)* **14**, 1483 (2002).

²³M. Sun, G. Zangari, M. Shamsuzzoha, and R. M. Metzger, *Appl. Phys. Lett.* **78**, 2964 (2001).

²⁴H. Q. Cao, Z. Xu, H. Sang, D. Sheng, and C. Y. Tie, *Adv. Mater. (Weinheim, Ger.)* **13**, 121 (2001).

²⁵Q. Xie, Z. Dai, W. W. Huang, J. B. Liang, C. L. Jiang, and Y. T. Qian, *Nanotechnology* **16**, 2958 (2005).

²⁶W. F. Brown, Jr., *Ann. N.Y. Acad. Sci.* **147**, 463 (1969).

²⁷J. I. Martin, J. Nogués, I. K. Schuller, M. J. Van Bael, K. Temst, C. Van Haesendonck, V. V. Moschalkov, and Y. Bruynseraede, *Appl. Phys. Lett.* **72**, 255 (1998).

²⁸Y. Peng, H. L. Zhang, S. L. Pan, and H. L. Li, *J. Appl. Phys.* **87**, 7405 (2000).

²⁹S. P. Li, A. Sanmad, W. S. Lew, Y. B. Xu, and J. A. C. Bland, *Phys. Rev. B* **61**, 6871 (2000).

³⁰J. Trygg, B. Johansson, O. Eriksson, and J. M. Wills, *Phys. Rev. Lett.* **75**, 2871 (1995).

³¹L. F. Liu, S. C. Mu, S. S. Xie, W. Y. Zhou, L. Song, D. F. Liu, S. D. Luo, Y. J. Xiang, Z. X. Zhang, X. W. Zhao, W. J. Ma, J. Shen, C. Y. Wang, and G. Wang, *J. Phys. D* **39**, 3939 (2006).