Magnetic-field-induced Synthesis of Co Filtering Film Consisting of Co Nanowires

Zhen Jin and Hao Li*
Department of Chemical Engineering, Huizhou University, Huizhou, Guangdong 516007, P. R. China

(Received June 11, 2009; CL-090558; E-mail: li.hi@mail.scut.edu.cn)

Co filtering film consisting of numerous compact Co nanowires with a diameter of ca. 10 nm was prepared by a magnetic-field-induced synthetic route. Room-temperature coercivity (*Hc*) of the Co filtering film measured with the applied magnetic field parallel and perpendicular to the film plane was 210 and 481 Oe, respectively, which was significantly higher than that of bulk Co film.

Magnetic thin films have drawn much attention due to their possible applications in many technological areas, such as magnetic data storage, spin valve, and microelectronic devices.[1,2] Particularly, as one of the most important magnetic metal materials, Co films have spurred intensive studies over the past several years.[3,4] So far, many physics- and chemistry-based methods have been developed for fabrication of two-dimensional Co thin film, including thermal deposition, pulsed laser deposition,[5] chemical vapor deposition (CVD),[6] ion-beam sputtering,[7] and electrodeposition,[8] as well as electroless methods in solution phase.[9] However, in most cases, these approaches are prone to produce Co film composed of granular Co particles. It is known that many properties and applications of magnetic thin films are highly related to their textures, surface morphology, and crystal structures. Recently, attempts have been made to improve the magnetic properties of the Co film by controlling the shape of nanosized subunits in the films. For example, Luo et al. synthesized unusual Co nanowire films with the assistance of a template and found the as-prepared films showed greatly enhanced coercivity, which is expected to have promising applications in many areas, such as magnetic storage devices and catalysts.[10] Therefore, it is of great significance to fabricate magnetic films with unusual and novel morphology and then find special properties of them for some interesting applications. However, despite significant progress in the preparation technology of metallic film, it is still a big challenge to fabricate Co thin film composed of shape-anisotropic Co nanocrystals.

Magnetic-field-assisted synthesis of shape-anisotropic magnetic nanostructures has been well documented.[11,12] In this study, we report the magnetic-field-induced synthesis of Co filtering film composed of Co nanowires, which was generated by chemical reduction of Co^{2+}–DCTA (1,2-diaminocyclohexane-*N*,*N*,*N*,*N*-tetraacetic acid) complexes in solution phase under a weak magnetic field.

In a typical synthetic procedure, 5 mmol of DCTA was added to a beaker containing 30 mL of NaOH solution (5 M) under stirring, followed by dropwise addition of 20 mL of $CoCl_2$ solution (0.2 M) to the mixed solution. Then, 10 mL of hydrazine hydrate solution (50%) and 20 mL of ethanol were added slowly to the above solution. Subsequently, the resulting solution was transferred into a Teflon®-lined stainless autoclave which was placed in a magnetic field with the magnetic field strength of ca. 0.07 T (Tesla) at the center of the Teflon® vessel. The magnetic field was provided by two magnets: one was put under the bottom of the autoclave and the other was put on the top of the autoclave. Finally, the autoclave, together with the two magnets, was kept in an air oven at 200 °C for 8 h. After the solvothermal reaction, the grey film, which adhered to the inner wall of the Teflon® cup, was carefully collected, washed, and then dried. X-ray diffraction (XRD) pattern was recorded using a Shimadzu/XD-3A X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). The morphology of the Co samples was studied using a Hitachi-4800 field emission scanning electron microscope (FE-SEM). Room-temperature magnetic hysteresis loops were measured using a Quantum Design MPMS XL-7 superconducting quantum interference device (SQUID) magnetometer.

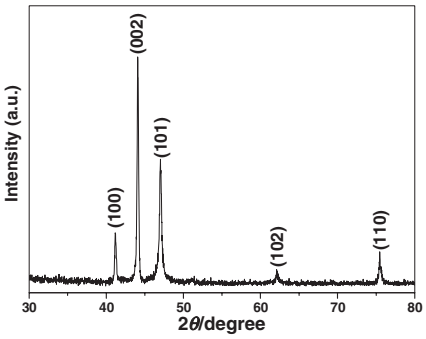

Figure 1. XRD pattern of the Co sample.

The XRD pattern of Co sample in Figure 1 shows five peaks at $2\theta = 41.5$, 44.3, 47.4, 62.5, and 75.8°, which correspond to the diffraction from the (100), (002), (101), (102), and (110) planes of hexagonal close-packed (hcp) Co (space group: $P6_3/mmc$(194); JCPDS: 05-0727, $a = 2.503$, $c = 4.060$ Å), respectively. No diffraction peaks of impurities, such as CoO and $Co(OH)_2$, are observed in the XRD pattern.

Figure 2a is the low-magnification SEM image of the as-prepared Co film, indicating that the film is very smooth and uniform. High-magnification SEM images (Figures 2b and 2c) show the Co film consisting of plenteous Co nanowires with an average diameter of ca. 10 nm, and many nanoscale holes can be observed in the film plane, which makes it look like an elaborate filtering film. Note that the Co nanowires in the film are randomly assembled without preferential orientation. It should be mentioned that ultrasonic treatment of 1 h could not break the film into separated nanowires and that the Co nanowires in the Co filtering film were actually fused into each other.

It was found that the magnetic field played a crucial role in determining the morphology of the final products. When no magnetic field was introduced during the synthesis, no Co film could be obtained in the inner wall of the Teflon® cup and the precipitated products were aggregated Co particles. This implied that the magnetic field was indispensable for the production of Co thin film. It was possible that with the assistance of a magnet-

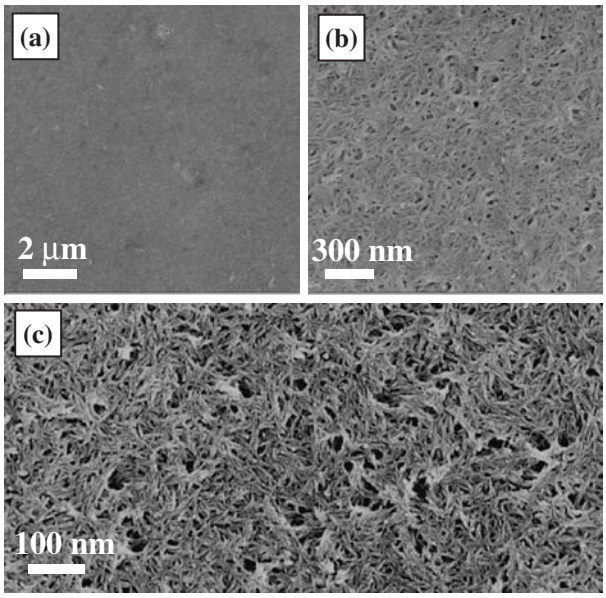

Figure 2. SEM images of the Co filtering film at different magnification.

ic field, Co nuclei and/or primary nanoparticles tended to aggregate together and deposit on the inner wall surface of the reactor to form the Co film when they arrived there. When a stronger external magnetic field (0.15 T) was applied, Co film composed of Co nanowires could also be achieved, but the average diameters of both the Co nanowires and the holes in the filtering film increased (See Figure S1 in Supporting Information).[16] This suggested that the sizes of nanowires and holes in filtering film may be tuned by changing magnetic intensity. The mechanism of formation of Co filtering film under the magnetic field in the synthesis is still unclear and further study is under way.

Figure 3 is the magnetic hysteresis loops of the Co filtering film measured at room temperature (300 K) with the applied field parallel and perpendicular to the film plane, which illustrates the typical ferromagnetic behaviors of the sample. The saturation magnetization values of the sample measured in the perpendicular direction and parallel direction were 153 and 139 emu g^{-1}, respectively. Note that the coercivity values of the Co filtering film measured in the perpendicular and parallel direction can reach 481 and 210 Oe, respectively. Compared to the bulk Co film which shows a low coercivity on the order of 10 Oe,[10] the as-prepared Co filtering film exhibits greatly enhanced coercivity. The coercivity is even higher than those of the recently reported two-dimensional Co nanofilm deposited on Alq_3 and oxidized Si substrate (less than 200 Oe).[13] The enhanced coercivity may be attributed to the high shape anisotropy of Co nanowires in the filtering film. A nonspherical magnetic polycrystalline specimen, such as nanowires and nanosheets, can possess net shape anisotropy, which will produce high coercivity.[14] However, the coercivity was still much lower than that of the Co film composed of well-arrayed Co nanowires with the diameter of 8 nm (385 and 890 Oe in the direction parallel and perpendicular to the film, respectively).[10] It was possibly due to the random assembly manner of the Co nanowires in the Co filtering film, which decreased the shape anisotropy as a total. In addition, the sintered interfaces between the Co nanowires will increase

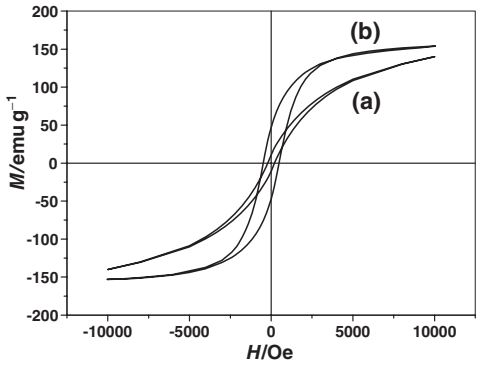

Figure 3. Room-temperature magnetic hysteresis loops of the Co filtering film with the magnetic field applied parallel (a) and perpendicular (b) to the film plane.

the average diameter of the Co nanowires, which will reduce the effect of shape anisotropy of the magnetic nanowires and thus resulted in a decrease in coercivity.[15]

In summary, hcp phase Co filtering film composed of Co nanowires with diameter of ca. 10 nm was prepared by a magnetic-field-induced approach, which showed enhanced coercivity compared with bulk counterpart. The as-prepared Co filtering film was novel in morphology and texure, so it was expected to show some special physical and chemical properties for some interesting applications. Moreover, this facile magnetic-field-induced route in solution phase may be extended to the preparation of some other magnetic film composed of shape-anisotropic magnetic nanocrystals, which is in progress in our laboratory.

References and Notes

1 T. Pan, G. W. D. Spratt, L. Tang, L. L. Lee, Y. Feng, D. E. Laughlin, *J. Appl. Phys.* **1997**, *81*, 3952.
2 K. Nagasaka, Y. Seyama, L. Varga, Y. Shimizu, A. Tanaka, *J. Appl. Phys.* **2001**, *89*, 6943.
3 S. J. Steinmuller, C. A. F. Vaz, V. Ström, C. Moutafis, D. H. Y. Tse, C. M. Gürtler, M. Kläui, J. A. C. Bland, Z. Cui, *Phys. Rev. B* **2007**, *76*, 054429.
4 Y. L. Iunin, Y. P. Kabanov, V. I. Nikitenko, X. M. Cheng, D. Clarke, O. A. Tretiakov, O. Tchernyshyov, A. J. Shapiro, R. D. Shull, C. L. Chien, *Phys. Rev. Lett.* **2007**, *98*, 117204.
5 H. L. Meyerheim, M. Przybylski, A. Ernst, Y. Shi, J. Henk, E. Soyka, J. Kirschner, *Phys. Rev. B* **2007**, *76*, 035425.
6 M. F. Chioncel, P. W. Haycock, *Chem. Vap. Deposition* **2005**, *11*, 235.
7 K. Horikiri, T. Kono, M. Morizumi, K. Shiiki, *J. Magn. Magn. Mater.* **2007**, *310*, 2604.
8 J. L. Bubendorff, E. Beaurepaire, C. Mény, J. P. Bucher, *J. Appl. Phys.* **1998**, *83*, 7043.
9 Å. Ekstrand, K. Jansson, G. Westin, *Chem. Mater.* **2005**, *17*, 199.
10 H. Luo, D. Wang, J. He, Y. Lu, *J. Phys. Chem. B* **2005**, *109*, 1919.
11 H. Niu, Q. Chen, H. Zhu, Y. Lin, X. Zhang, *J. Mater. Chem.* **2003**, *13*, 1803.
12 H. Li, S. Liao, *J. Magn. Magn. Mater.* **2009**, *321*, 2566.
13 I. Bergenti, A. Riminucci, E. Arisi, M. Murgia, M. Cavallini, M. Solzi, F. Casoli, V. Dediu, *J. Magn. Magn. Mater.* **2007**, *316*, e987.
14 D. L. Leslie-Pelecky, R. D. Rieke, *Chem. Mater.* **1996**, *8*, 1770.
15 K. Nielsch, R. B. Wehrspohn, J. Barthel, J. Kirschner, U. Gösele, S. F. Fischer, H. Kronmüller, *Appl. Phys. Lett.* **2001**, *79*, 1360.
16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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