Fabrication and Magnetic Properties of CoPd Nanowire Arrays

Jing-Bo Ding, Dong-Huan Qin, Yi Huang, Lin Cao, and Hu-Lin Li

(Submitted 21 February 2003; in revised form 10 April 2003)

Highly ordered CoPd nanowire arrays from a co-ordination complex electrolyte solution have been fabricated by alternating current electrodeposition onto nanoporous anodic alumina. Structural and magnetic properties of the arrays were investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM), x-ray diffraction (XRD), and vibrating sample magnetometer (VSM). A coercivity of about 1 kOe and a fair loop squareness has been obtained in the out-of-plane direction, which is promising for perpendicular magnetic recording.

Keywords CoPd nanowire arrays, high density recording, porous anodic alumina

1. Introduction

Magnetic patterned arrays have recently received considerable attention for their potential in high-density magnetic data storage device, magneto-electronic, and microwave applications.[1] Due to large aspect ratio and consequent high shape anisotropy, such materials have a higher perpendicular anisotropy than in bulk state or as thin films, which are suitable for perpendicular magnetic recording. In patterned array media, each single-domain nanosized particle (so-called nanomagnet) could be defined as one bit of binary information. Because one bit corresponds to a single domain particle, in principle, high data storage density can be achieved by reducing the size and the spacing of magnetic particles. In contrast to the conventional longitudinal recording media, magnetic patterned array media can achieve a higher density and more satisfactory signal-to-noise ratio with fewer limitations such as thermal instability and superparamagnetic limit of the magnetic particle. Chou[2] achieved 10 nm features with 40 nm period Ti/Cu dots with nanolithography corresponding to 62 Gdots/cm^2. Many investigations[1,3-6] have been undertaken to fabricate such magnetic nanowire arrays: electron beam lithography, imprint technology, nuclear track etching, and electro-deposition methods.

As the pore density is high, the pore distribution is uniform and the diameter of the pores is easily controlled by anodizing conditions. Porous anodic alumina (PAO) is an attractive template for fabricating nanowires or nanotubes. Up to now, nanomagnet arrays such as Fe, Co, Ni,[7-10] and their alloys are fabricated based on a PAO template and their magnetic properties are investigated. Although CoPd nanostructure arrays have been widely investigated,[11] few studies have examined CoPd arrays fabricated by using electrodeposition of Co-Pd salt solution in PAO as there is a great difference between the deposition potential of Co^{2+} and that of Pd^{2+}, and co-deposition of Co^{2+} and Pd^{2+} cannot be achieved unless some type of complexing agent is added to pull the deposition potentials of Pd^{2+} and Co^{2+} together. In this paper, we report on a new way to prepare CoPd nanowire arrays. The structure and magnetic properties of CoPd nanowire arrays were characterized by x-ray diffraction (XRD) and vibrating sample magnetometer (VSM). High perpendicular anisotropy was found in such media and might be useful in perpendicular magnetic recording.

Jing-Bo Ding, Dong-Huan Qin, Yi Huang, Lin Cao, and **Hu-Lin Li,** Department of Chemistry, Lanzhou University, Lanzhou, China, 730000, GanSu, P.R. China. Contact e-mail: lihl@lzu.edu.cn.

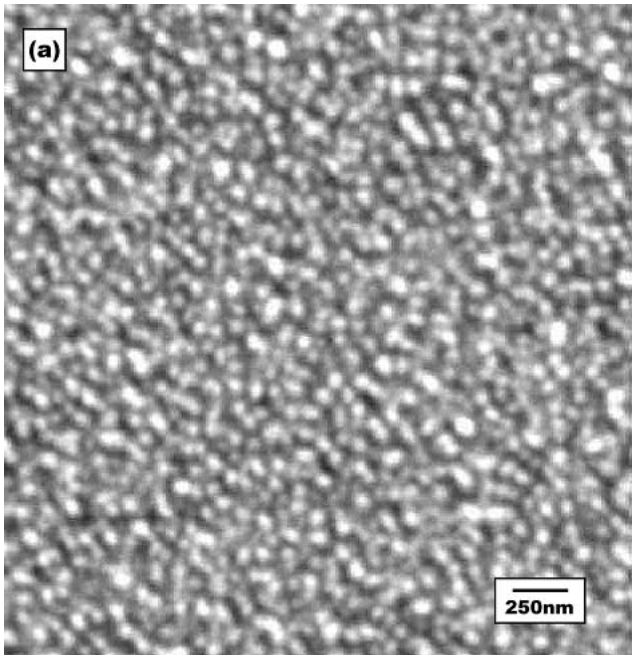
2. Experimental Procedure

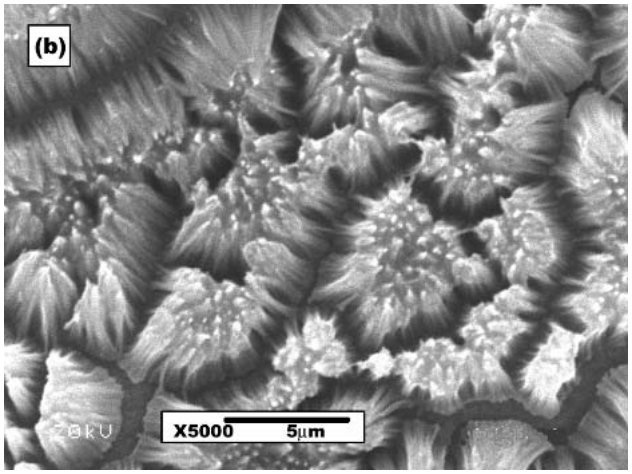
2.1 CoPd/PAO-array Fabrication

Patterned PAO templates were prepared by anodic oxidation of Al foil with purity of 99.999% in oxalic acid solution under a two-step anodizing process. The whole process can be seen in our previous works.[12,13] The diameter is about 50 nm and pore density is about 10^{11} cm^{-2} in the resulting PAO template. As the deposition potential of Co^{2+} is much lower than that of Pd^{2+}($E^{\Phi}_{Co^{2+}/Co} = -0.277$V, $E^{\Phi}_{Pd^{2+}/Pd} = 0.987$V), the co-deposition of Co^{2+} and Pd^{2+} will be impossible unless the deposition potential of Pd^{2+} decreases. In this experiment, a solution containing Co^{2+} and Pd^{2+} ions was prepared as following: 0.129 g $PdCl_2$ was dissolved into 20 ml distilled water with several drops of hydrochloric acid. Then 0.175 g $CoCl_2 \cdot 6H_2O$ was added into the solution using a magnetic stirrer. The resulting solution was added to 20 ml ethylendiamine slowly under stirring condition. The complex reactions between Co^{2+}, Pd^{2+}, and ethylendiamine are listed below:

$$Co^{2+} + NH_2CH_2CH_2NH_2 \rightarrow [Co(NH_2CH_2CH_2NH_2)]^{2+}$$
$$Pd^{2+} + NH_2CH_2CH_2NH_2 \rightarrow [Pd(NH_2CH_2CH_2NH_2)]^{2+}$$

After the complex reactions the deposition potential of Co^{2+} was almost the same as that of Pd^{2+}, thus achieving co-deposition of Co^{2+} and Pd^{2+}. The pH value of electrolyte was adjusted to 3.6-4.8 with HCl. CoPd nanowire arrays were fabricated by AC electro-deposition at 25 °C with carbon as the counter electrode and a PAO template as the working elec-





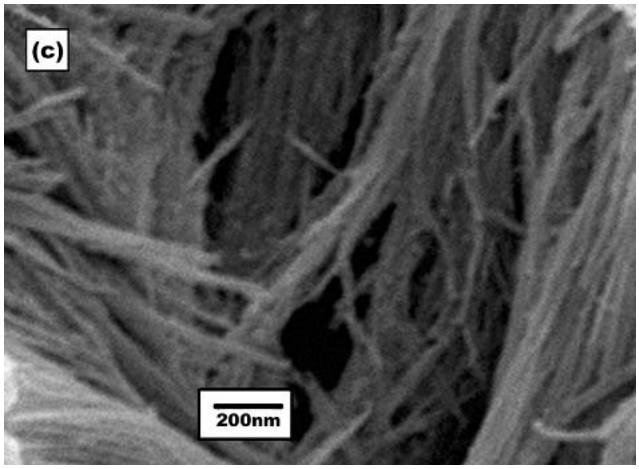
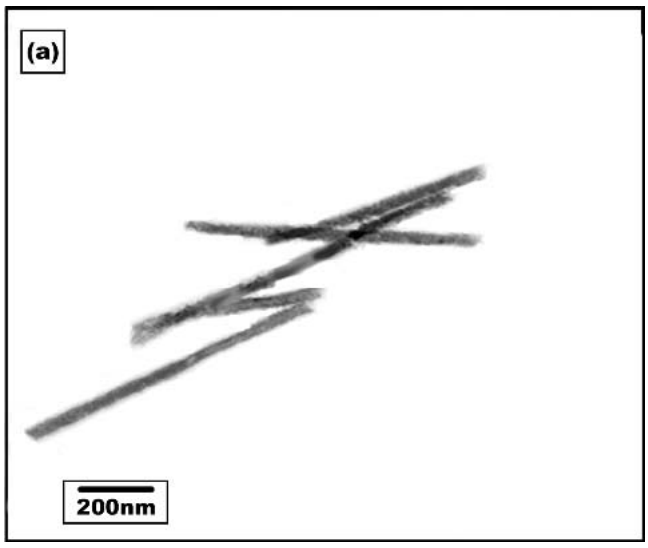


Fig. 1 SEM images of CoPd nanowire arrays after partly dissolving the PAO substrate in mixed acid solution for different time: **(a)** 30 min; **(b)** 60 min; and **(c)** 90 min



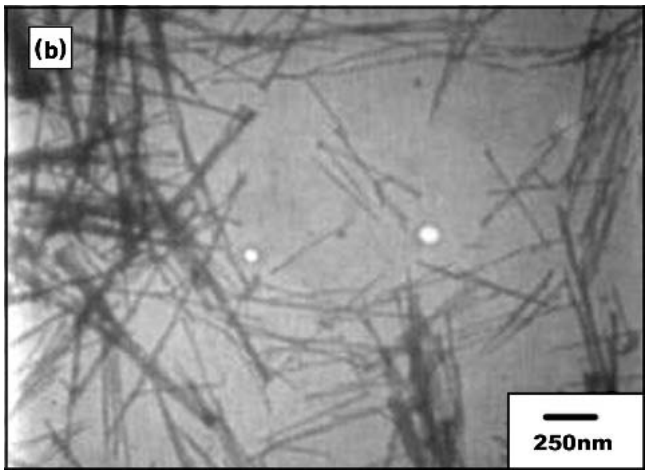


Fig. 2 TEM image of 50 nm CoPd alloy nanowires with PAO template removed **(a)** small area TEM image; and **(b)** large area TEM image

trode. The deposition potential was selected to be 9.0 V ac and frequency was 200 Hz. We found that CoPd nanowire arrays could not be obtained at too high deposition potential (up to 10 V). This could be due to the fact that ethylendiamine centralized around PAO quickly and reacted with PAO, then the PAO was dissolved and CoPd alloy was deposited on Al sheet directly. The composition of the samples was checked by Atomic Absorption Spectroscopy (AAS) (Hitachi, 180-80, Japan) and the atom ratio between Co and Pd in the sample is 3:7.

To obtain transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of CoPd arrays, the samples were partially or completely dissolved in a 0.1 M NaOH aqueous solution.

2.2 Experimental Instrument

The microstructure, composition, and magnetism of the samples were characterized by SEM (JOEL JSM5600LVSEM, Japan), TEM (Hitachi 600, Japan), x-ray diffraction (XRD,

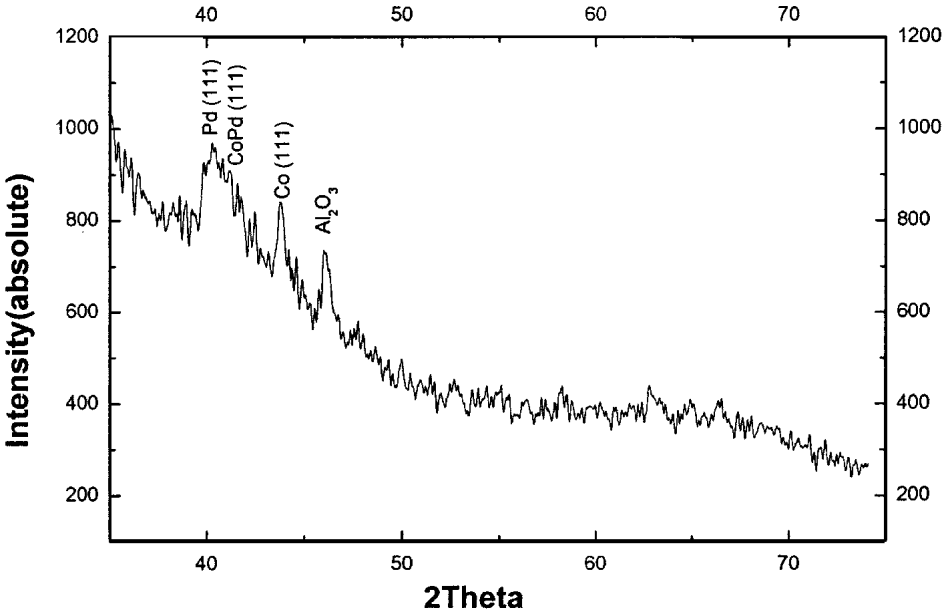


Fig. 3 Powder Cu-Kα XRD patterns of Co, Pd, and CoPd alloy nanowire arrays (the peak of CoPd (111) overlaps partly with the peak of Pd (111))

Rigaku, Model D/max 2400, Japan; Cu *K*α radiation, λ = 1.54184Å), and vibrating sample magnetometer (VSM, VSM-5s-15, Japan).

3. Results and Discussion

3.1 Structure Characteristic

Figure 1(a), (b), and (c) shows SEM micrographs of CoPd nanowire arrays. To do this, CoPd/PAO had been dipped into mixed acid solution (3.5vol%H_3PO_4-45g/lCrO_3) for 30, 60, and 90 min, respectively, to partially dissolve the aluminum oxide layer. CoPd nanowires fill the pores of PAO very well (Fig. 1a), and with the dissolving time increasing, the nanowires are displayed. It is obvious that the nanowires are parallel to one another and the diameters of all nanowires are almost the same as those of PAO pores. To probe the structure characteristic of CoPd nanowires, the aluminum oxide layer was dissolved completely in a 0.1 M NaOH aqueous solution. Small area and large area of TEM images of CoPd nanowires are shown in Fig. 2(a) and (b), from which we can see that the diameter is about 50 nm while the length is up to 1 μm. The aspect ratio of the wires exceeds 20, so that high shape anisotropy was obtained in such CoPd nanowire arrays. Selected area XRD also showed that the wire was composed of many microcrystals.

The x-ray diffraction (XRD) patterns of Co, Pd, and CoPd nanowire arrays are shown in Fig. 3, where the diffraction peaks can be assigned to Co [111], Pd [111], and CoPd [111] alloy. The peaks are rather weak and no hexagonal HCP Co peaks were found; such peaks are usually strong and narrow in bulk Co and Co arrays prepared by electrodeposition.[14] The disappearance of HCP Co can be explained by the rapid growth of these nanowires and the effects of Pd^{2+} during electrodeposition. The crystal matching between Co particle and Pd particle makes the alloy phase form, which has been also confirmed by Scarani et al.[15] who prepared CoCu alloy nanowires. The presence of Co (111) and Pd (111) peaks implies that the crystallization of CoPd was not perfect, which will reduce the magnetic properties of the alloy arrays. Although we annealed the samples at different temperatures, almost no change was found from the XRD and VSM results.

3.2 Magnetic Properties of CoPd Arrays

Figure 4(a) and (b) shows representative hysteresis loops of CoPd/PAO nanowire arrays measured with an applied field (10 kOe) parallel and perpendicular to the wire axis at room temperature. The squareness (Mr/Ms) is as high as 0.74 and the coercivity is 1000Oe when the applied field is parallel to the axis of nanowire arrays (Fig. 4a). However, the coercivity is only 500Oe and the squareness is about 0.21 when the applied field is perpendicular to the axis of nanowire arrays (Fig. 4b). We can conclude that the easy magnetization direction is parallel to nanowire arrays while hard magnetization direction is perpendicular to CoPd arrays. This means that the magnetic moment of CoPd alloy arrays is oriented along the nanowire arrays, and every nanowire can be regarded as a single domain structure. The CoPd/PAO arrays show high perpendicular magnetic characteristics.

The principal origin of perpendicular anisotropy is due to the competition between magnetocrystalline anisotropy and shape anisotropy. In this case, because the aspect ratio of CoPd nanowire is very high (up to 20), magnetocrystalline anisotropy plays a minor role to the magnetic anisotropy. The strong magnetic anisotropy found in the localized CoPd alloy arrays is mainly predominated by shape anisotropy with the easy axis parallel to nanowires. At a first approximation, we can therefore assume that the magnetic properties of CoPd alloy arrays are governed by shape anisotropy. The shape anisotropy field estimated by infinite cylinder ($H_A = 2\pi M_s$) is about 3100Oe.

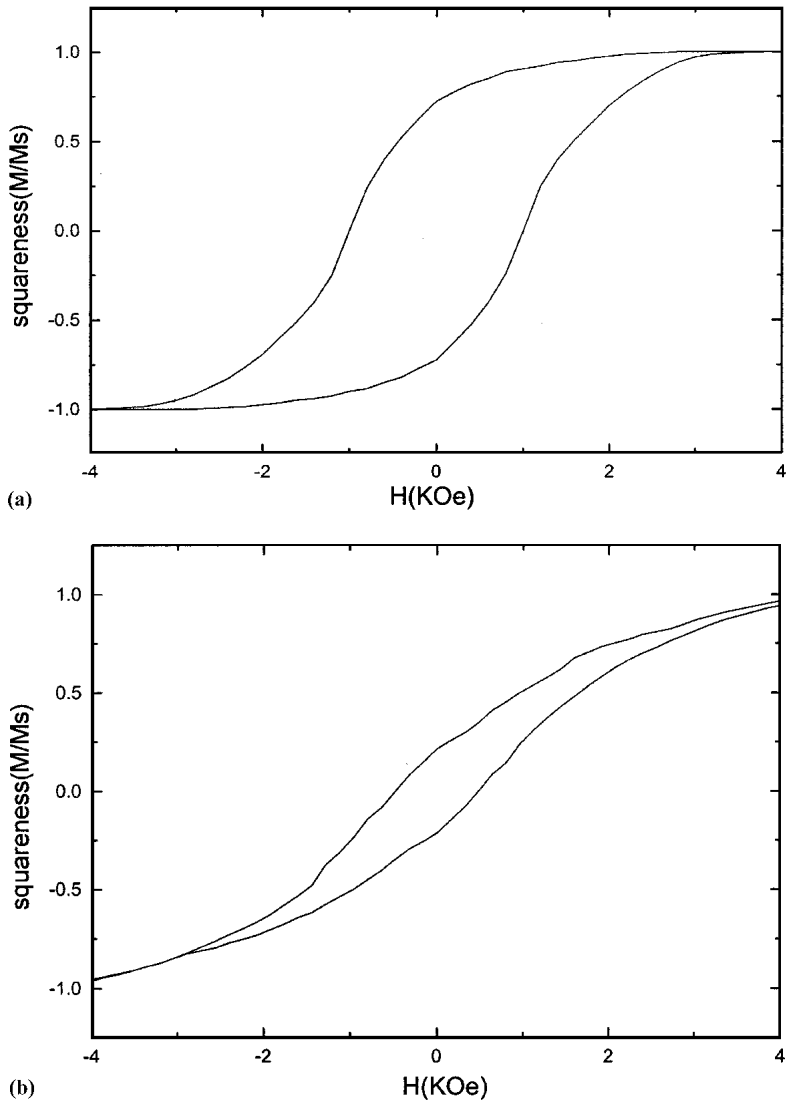


Fig. 4 Magnetic hysteresis loops for the as-deposited samples **(a)** out of plane: with external field H parallel to the long axis of nanowires; **(b)** in-plane: with external field H perpendicular to the long axis of nanowires

However, the coercivity is only about 1000Oe in the applied field parallel to nanowire arrays in our work. The main reason can be explained in several ways. First, according to infinitely long cylinders model proposed by Stoner and Wohlfarth,[16] the demagnetization along nanowire arrays should be zero. In fact, the magnetic behavior is very complicated in CoPd nanowires; many factors cannot be neglected such as various kinds of imperfection of real particles, the effects of neighboring nanowires, and intergranular couple between the alloy grains. So the coherent rotation process based on such an idealized model could not explain the behavior of hysteresis loops in magnetic nanowire arrays and some researchers propose a new model—the localize rotation model.[17] In our previous work[14] we found that every single nanowire represented a single domain structure and each single domain was surrounded by six single domains whose directions were in opposition. The effects of neighboring wires as effective-field is corrected by $\Delta H = -\Delta NM$[9] (ΔN is a function of packing density). This demagnetizing-field correction will shear the hysteresis loop and so that decrease the coercivity or the perpendicular anisotropy. Second, at low Co concentrations, Co-Pd alloys are known to have large negative anisotropy constants K_1 and K_2, resulting in a <111> easy axis,[18] which is also found in our XRD data. The <111> axis is parallel to nanowire arrays. However, the lower degree of crystallinity and internal stress that were formed during rapid deposition will decrease perpendicular anisotropy and induce anisotropy, which causes a departure from the easy axis. Based on the localized reversal model in which many factors are taken into account, H_c can be simply expressed phenomenologically as follows:[9]

$$H_c = \alpha \frac{2K_u}{M_s} - N_{eff}M_s$$

α is a parameter that depends on grain orientation and reversal mechanism and N_{eff} is an effective demagnetizing factor that is

related to magnetostatic interactions. According to the calculation H_c value is only about 20-30% of H_A and less than that estimated by the infinite cylinder model. Our results confirm with this model very well.

4. Conclusion

In summary, patterned CoPd nanowire arrays were fabricated by AC electrodeposition with PAO as template. TEM, SEM, XRD, and VSM were used to characterize the structure and magnetic properties of such CoPd nanostructure arrays. High perpendicular anisotropy was found in such media and the hysteresis loop was explained by nucleation-propagation localized reversal model. As the density of CoPd nanowires was very high, it was very attractive in high-density perpendicular recording if one single nanowire represented one bit of binary data.

Acknowledgment

This work is supported by the National Natural Science Foundation of China (No. 60171004).

References

1. L. Kong and S.Y. Chou: "Effects of Bar Length on Switching Field of Nanoscale Nickel and Cobalt Bars Fabricated Using Lithography," *J. Appl. Phys.,* 1996, *80,* pp. 5205-08.
2. S.Y. Chou: "Patterned Magnetic Nanostructures and Quantized Magnetic Disks," *IEEE Trans. Magn. MAG*-85, 1997, pp. 652-71.
3. S.Y. Chou, M.S. Wei, and P.B. Fischer: "Single-Domain Magnetic Pillar Array of 35 nm Diameter and 65 Gbits/in^2 Density for Ultrahigh Density Quantum Magnetic Storage," *J. Appl. Phys.,* 1994, *76,* pp. 6673-75.
4. G.A. Gibson and S. Schultz: "Magnetic Force Microscope Study of the Micromagnetics of Submicrometer Magnetic Particles," *J. Appl. Phys.,* 1993, *73,* pp. 4516-21.
5. R.M.H. New, R.F.W. Pease, and R.L. White: "Physical and Magnetic Properties of Submicron Lithographically Patterned Magnetic Islands," *J. Vac. Sci. Technol. B,* 1995, *13,* pp. 1089-94.
6. S. Manalis, K. Babcock, J. Massie, and V. Elings: "Submicron Studies of Recording Media Using Thin-Film Magnetic Scanning Probes," *Appl. Phys. Lett.,* 1995, *66,* pp. 2585-87.
7. D.J. Sellmyer, M. Zeng, and R. Skomski: "Magnetism of Fe, Co and Ni Nanowires in Self-Assembled Arrays," *J. Phys.: Condens. Matter,* 2001, *25*, R433-60.
8. L. Menon, M. Zheng, H. Zeng, S. Bandyopadhyay, and D.J. Sellmyer: "Size Dependence of the Magnetic Properties of Electrochemically Self-Assembled Fe Quantum Dots," *J. Electron. Mater.,* 2000*, 29,* pp. 510-14.
9. H. Zeng, M. Zheng, R. Skomski, and D.J. Sellmyer: "Magnetic Properties of Self-Assembled Co Nanowires of Varying Length and Diameter," *J. Appl. Phys*., 2000, *87,* pp. 4718-20.
10. M. Zheng, L. Menon, H. Zeng, Y. Liu, S. Bandyopadhyay, R.D. Kirby, and D.J. Sellmyer: "Magnetic Properties of Ni Nanowires in Self-Assembled Arrays," *Phys. Rev. B,* 2000, *62,* pp. 12282-86.
11. E. Gan'shina, V. Guschin, S. Kirov, O. Shabanova, and A. Tselev: "Magneto Optical Properties of Alloy Films Co–Pd With Perpendicular Magnetic Anisotropy," *J. Magn. Magn. Mater.,* 1999, *203,* pp. 244-46.
12. S.L. Pan, D.D. Zeng, and H.L. Li: "Preparation of Ordered Array of Nanoscopic Gold Rods by Template Method and Its Optical Properties," *Appl. Phys. A,* 2000, *70,* pp. 637-40.
13. C.W. Wang, Y. Peng, S.L. Pan, and H.L. Li: "Mössbauer Study of Magnetic Anisotropy of α-Fe Patterned Nanowire Arrays," *Acta Phys. Sin.,* 1999, *11,* pp. 2146-50.
14. D.H. Qin, M. Lu, and H.L. Li: "Magnetic Force Microscopy of Magnetic Domain Structure in Highly Ordered Co Nanowire Arrays," *Chem. Phys. Lett.,* 2001, *350,* pp. 51-56.
15. V. Scarani, B. Doudin, and J.P. Ansermet: "The Microstructure of Electrodeposited Cobalt-Based Nanowires and Its Effect on Their Magnetic and Transport Properties," *J. Magn. Magn. Mater*., 1999, *205,* pp. 241-48.
16. E.C. Stoner and E.P. Wohlfarth: "A Mechanism of Magnetic Hysteresis in Heterogeneous Alloys," *Phil. Trans. R. Soc. A,* 1948, *240,* pp. 599-642.
17. R. Skomski, H. Zeng, and D.J. Sellmyer: "Incoherent Magnetization Reversal in Nanowires," *J. Magn. Magn. Mater.,* 2002, *249,* pp. 175-80.
18. D.M.S. Bagguley and J.A. Robertson: "Resonance and Magnetic Anisotropy in Dilate Alloys of Pd, Pt With Fe, Co and Ni," *J. Phys. F.,* 1974, *4,* pp. 2282-96.