Available online at www.sciencedirect.com
SCIENCE DIRECT®
Chemical Physics Letters 374 (2003) 661–666
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

A study of magnetic properties: Fe_xCo_{1-x} alloy nanowire arrays

Dong-Huan Qin [a], Yong Peng [b], Lin Cao [a], Hu-Lin Li [a,*]

[a] Department of Chemistry, Lanzhou University, Lanzhou, Gansu 730000, PR China
[b] Joule Physics Laboratory, Institute for Materials Research, The University of Salford, Greater Manchester M5 4WT, UK

Received 19 March 2003; in final form 8 May 2003

Abstract

Highly ordered arrays of Fe_xCo_{1-x} ($x = 0$–1.0, nominally) alloy nanowire were prepared by electrodepositing Fe^{2+} and Co^{2+} into the porous anodic aluminum oxide (PAO) templates. XRD experiments proved that the crystal structure of alloy nanowire was bcc. The magnetic properties of Fe_xCo_{1-x} nanowire arrays showed strong magnetic anisotropy, whose easy axis was parallel to the nanowires. Suitable annealing temperature caused coercivity and squareness of sample to increase rapidly, which was higher than those of as-prepared samples. The change in coercivity and squareness of all samples was discussed in detail. The magnetic reversal mechanism may be attributed to localized nucleation based on Zeng's theory [J. Appl. Phys. 87 (2000) 4718].

1. Introduction

Perpendicular magnetic recording system is one of the most promising candidates to realize the extremely high-density recording (HDR) due to its superior thermal stability and high track density [1]. One such technology to prepare sample with high perpendicular magnetic anisotropy is based on template method. There have been considerable efforts in the investigation of large area highly ordered ferromagnetic nanowire for the purpose of application in ultra-high density perpendicular magnetic recording devices [2–4]. Different from conventional magnetic recording materials, the nanowires are embedded in non-magnetic media and there are only two stable opposite magnetization directions due to the high shape anisotropy of the nanowires. Such arrays are also referred to as quantized magnetic disks (QMD) [5]. Chou [6] obtained a recording density about of 400 Gbits/in [1] in Ti/Au dots with 40-nm pitch fabricated using nanoimprint lithography and lift-off.

PAO has a highly oriented porous structure with very uniform and nearly parallel pores that can be organized in an almost precise hexagonal structure. These merits make it become an ideal template for preparing metal or semiconductor

* Corresponding author. Fax: +86-931-891-2582.
E-mail addresses: qindonghuan@sohu.com (D.-H. Qin), lihl@lzu.edu.cn (H.-L. Li).

0009-2614/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0009-2614(03)00809-1

nanowires. To date, semiconductors such as CdS [7] and GaAs [8] arrays have been prepared by using PAO as a template successfully. For magnetic arrays, many early studies were mainly concerned with single metal arrays such as Co [9], Fe [10], and Ni [11] nanowires. However, recently, attention has been shifted towards preparing alloy arrays such as FeCo [12] or FeNi [13] and understanding of magnetization process. It is easy to change the coercivity and squareness of recording media to reach the requirements of real device by adjusting the component of alloy.

In contrast to Fe, Co or Ni, Co_xFe_{1-x} alloy has high saturation magnetization, low magnetic crystalline anisotropy K_1 (the fist magnetic crystalline anisotropy constant) and high Curie temperature, which is more suitable for high temperature applications. In the range of $0.3 < x < 0.7$, Fe_xCo_{1-x} alloys in bulk material or thin film undergo a phase transformation from a disordered bcc structure to the ordered CsCl structure below 730 °C. The ordered alloy shows excellent soft magnetic properties with negligible magnetocrystalline anisotropy K_1 [14]. So the magnetic properties of Fe_xCo_{1-x} nanowire arrays are mainly predominated by shape anisotropy of the nanowires. The shape anisotropy of the magnetic nanowires can be estimated by the simplest Stoner–Wohlfarth model [15] $K_s = (\mu_0/4)M_s^2$, and the corresponding anisotropy field $H_c \approx H_A = 2K_s/\mu_0 M_s = \mu_0 M_s/2$, which shows that H_c is linear with M_s. Therefore, if we want to improve the coercivity of materials, the good way is to improve M_s of materials or use materials with large M_s and weak crystalline anisotropy, such as Fe_xCo_{1-x} alloy. In this Letter, we report our work on fabrication and annealing effects on magnetic characterization of Fe_xCo_{1-x} nanowire arrays. Further, localized nucleation model is adopted to explain the reversal process in alloy arrays.

2. Experimental

Highly ordered PAO templates with pore diameter of about 50nm were prepared by anodic oxidation of 99.999% pure Al sheet in oxalic acid solution under two-step anodizing process. The first process was carried out at a constant voltage of 40 V in 0.2 M oxalic acid solution at 0 °C for 3 h. Secondly, the oxide film was dissolved in 0.2 M $H_2Cr_2O_4$, 0.4 M H_3PO_4 at 60 °C, then, the patterned aluminum substrate was anodized again like the first process. The preparing process can be seen in our previous work [16] and other group's work [17]. The diameter is about 50 nm and pore density about 10^{10} cm^{-2} in the resulting PAO template prepared by two-step anodization (see Fig. 1).

The electro-deposition was carried out by AC voltage with graphite rod as counter-electrode and PAO template with aluminum plate as working electrode at room temperature. The electrolyte solution consisted of 1.2–11.8 g/l $CoSO_4 \cdot 7H_2O$, 1.2–11.8 g/l $FeSO_4 \cdot 7H_2O$, 30 g/l boric acid and 1.5 ascorbic acid. The voltage and the frequency of sine wave used in electro-deposition were 11.5 V and 200 Hz, respectively. We found that the electro-deposition velocity of Fe^{2+} is almost the same as that of Co^{2+} during AC electrodeposition process and slower than that of Co^{2+} in the case of DC electro-deposition. Based on these values, the component of Fe_xCo_{1-x} alloy nanowires can be easily controlled by adjusting the relative concentration of Co^{2+} and Fe^{2+} in electrolyte.

2.1. Instruments

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to

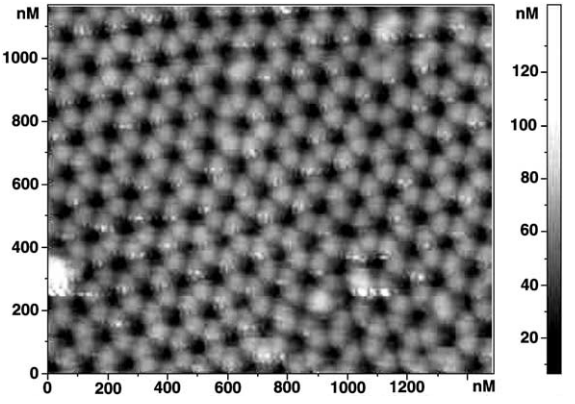

Fig. 1. AFM image of PAO template.

characterize the morphology of nanowire arrays, while atomic absorbed spectrum device, X-ray diffraction (XRD, Rigaku, Model D/max 2400; Cu K_α radiation, $\lambda = 1.5418$ Å) was used to investigate the content and crystalline structure of the samples, respectively. Magnetic properties of the as-prepared and annealing samples were tested by a vibrating sample magnetometer.

To obtain morphology structure of alloy arrays, the sample was dipped into a solution of 3.5 vol% H_3PO_4 and 45 g/l CrO_3 for different times. For SEM images it was 30 min, while for TEM images it took about 3 h to dissolve the alumina matrix completely and washed by distilled water several times.

3. Results and discussion

Fig. 2a shows the SEM images of arrays of $Fe_{0.3}Co_{0.7}$ nanowires in PAO template. One can see that a high degree of pore filling rate (up to 0.9) is obtained from the electro-deposition. TEM image (Fig. 2b) also shows that the nanowires prepared by PAO template synthesis are of regular size and are continuous and parallel to each other. The diameter is about 50 nm while length is up to 1 μm, so the aspect ratio (length to diameter) is up to 50. Hence, the aspect ratio of which is about 80, the shape anisotropy of Fe_xCo_{1-x} nanowire arrays is very high in our case. Selected-area electron diffraction (SAED) reveals that Fe_xCo_{1-x} alloy arrays are composed of polycrystalline structure.

The X-ray diffraction (XRD) spectra of the Fe_xCo_{1-x} (with x range from 0.1 to 0.9) nanowire arrays are shown in Fig. 3. From this figure, the main diffraction peaks can be assigned to FeCo (1 1 0), FeCo (2 1 1), the same as that of FeCo thin film, and the other diffraction peaks of FeCo alloy cannot be found in most of our spectra. The other peaks ($2\Theta < 40$) can be assigned to the peaks of alumina.

Fig. 4 shows dependence of the coercivity H_c and squareness (M_r/M_s) on the Fe composition of the alloy arrays before annealing. It can be seen that with an increase of x (from 0 to 0.2), the coercivity (the applied field parallel to nanowire ar-

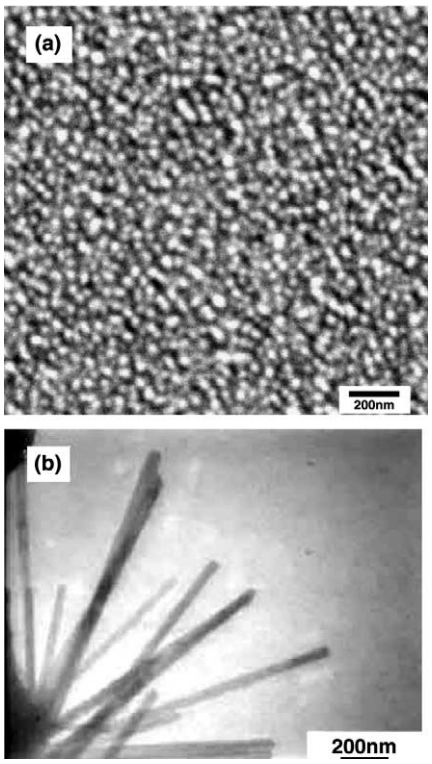

Fig. 2. (a) SEM image of $Fe_{0.4}Co_{0.6}$ nanowire arrays. The bright dots are the filled pores. EDAS of the surface of the samples shows 40 at.%; 60 at.% Fe; (b) TEM image of 50 nm FeCo alloy nanowires arrays with PAO templates removed.

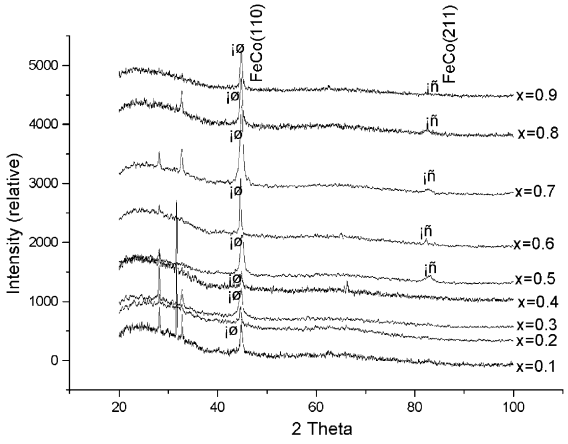

Fig. 3. X-ray spectra of Fe_xCo_{1-x} nanowire arrays with different Fe components.

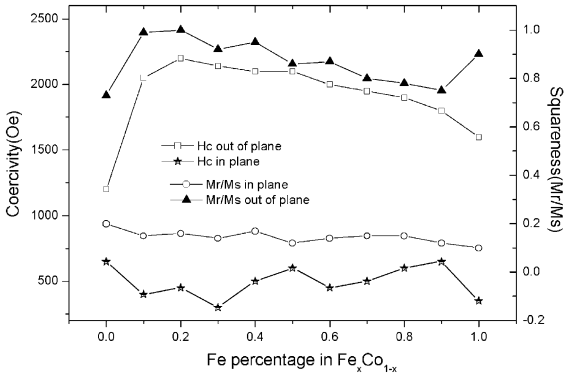

Fig. 4. Coercivity (H_c) and squareness vs. Fe component in as-deposited samples: (//) external field parallel to nanowire axis; ($\perp$) external field perpendicular to nanowire axis.

rays) firstly increases from 1200 to 2300 Oe, then drops down almost linearly with increasing x (from 0.2 to 0.9). Finally it drops down to 1600 Oe in the case of pure Fe. However, the coercivity is less than 600 Oe and squareness is less than 0.2 when the applied field is perpendicular to the nanowire arrays, which shows that such Fe_xCo_{1-x} arrays have high perpendicular anisotropy with their easy axis being parallel to nanowire arrays. The change of the coercivity H_c with the Fe content is closely related to the variation of microstructure factors. Due to the rapid deposition of Fe^{2+} and Co^{2+} into the PAO template, intrinsic stress and defects are high and a disordered bcc structure are found in the samples. Disordered bcc structure and small grain size in Fe_xCo_{1-x} alloy exhibits a relatively large negative K_1, causes a high H_c due to the magneto-crystallize anisotropy from the disordered sample. However, the value of K_1 in these samples is still much lower than that of their shape anisotropy, so that the coercivity is mainly dominated by the shape anisotropy (K_s). With high M_s in Fe_xCo_{1-x} alloy, large coercivity is expected in FeCo alloy nanowire. The drop down of H_c when x is up to 0.2 can be explained by high stress tension in the as-prepared sample and the decrease of M_s in the material. In addition, Co tends to form hcp structure when the concentration of Co^{2+} is low during electro-deposition, which had been conformed by Scarani [18] who prepared CoCu alloy nanowire arrays. The hcp Co has its easy axis perpendicular to nanowires and decreases anisotropy along nanowire arrays. So coercivity in Fe_xCo_{1-x} arrays drops down in the case of high Fe content.

In order to study the annealing effects on Fe_xCo_{1-x} alloy nanowire arrays, all samples are annealed at different temperatures 300, 400, 450, 500, 550 and 600 °C, respectively, with low vacuum pressure of 10^2 Pa in Ar atmosphere. It is found that the coercivities of all samples have increased after annealing (Fig. 5a). The coercivity increases linearly when annealing temperature ranges from 300 to 500 °C, however, too high annealing temperature (above 550 °C) will deteriorate the magnetic properties of the samples. At low annealing temperature and low Fe content, the M_r/M_s of all samples (Fig. 5b) does not change a lot and maintain at a very high level (at least 0.75), which shows that the samples could keep their good perpendicular recording properties. When Fe content increases, the squareness drops down rapidly to a very low value of 0.6. The samples

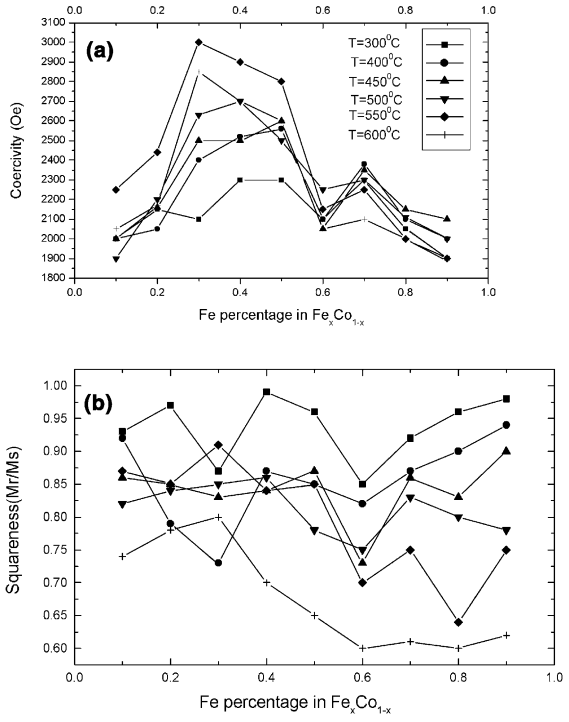

Fig. 5. (a) Coercivity vs. annealing temperature; (b) squareness vs. annealing temperature, whose applied field is 16 kOe.

with different Fe contents annealing at high temperature (about 600 °C) get the lowest squareness (below 0.7) and coercivity. In addition, we have found that coercivity as high as 3000 Oe and squareness of about 0.91 can be obtained in $Fe_{0.3}Co_{0.7}$ annealing at 550 °C compared to 2200 Oe for a non-annealed sample. We propose that the change of magnetic properties of Fe_xCo_{1-x} after annealing is related to microstructure change during annealing process. Firstly, thermal annealing relieves the internal stress in the samples induced by rapid deposition of Fe^{2+} and Co^{2+} and a high degree of crystallinity is obtained. So the M_s of annealed samples is higher than its as-deposited state. As the M_s increases in Fe_xCo_{1-x} alloy arrays after annealing at some temperature, high H_c is expected. Secondly, there is a large mismatch between the thermal expansion coefficients (α) of Fe_xCo_{1-x} alloy and alumina. The α (about 14.0×10^{-6} K^{-1}) of FeCo alloy is much higher than that of PAO (about 6.0×10^{-6} K^{-1}). So, it is not hard to imagine that FeCo alloy tends to expand along the wire axis during annealing and form column structure with easy axis along nanowire arrays, which will improve shape anisotropy at local region. On the other hand, some of the Fe or Co atoms does not form fcc FeCo alloy during annealing, which may act as defects and prevent the movement of domain wall, then the coercivity will be improved in the samples. Certainly, there are also microstructure changes such as the change of K_1 (the first magneto-crystalline anisotropy) and phase segregation due to Fe/Co short-range order, which had been found in FeCo thin film [19]. While annealing at high temperature (up to 500 °C), internal stress will increase and the alumina distort. The pore of PAO template will deviate from its original place and the shape anisotropy will drop down. Furthermore, unavoidably, Fe will react with O_2 existed in anodic aluminum oxide at high temperature as the Fe content is high in the samples, which will deteriorate M_s and decrease perpendicular anisotropy in the alloy arrays.

As for the reversal process in thin magnetic nanowire arrays, many early work [20,21] involved competition between shape anisotropy and magneto-crystalline anisotropy in nanowire arrays. Recently, Skomski et al. [22] pointed out that the reversal process in thin magnetic nanowire with small diameter should not be simply considered as coherent rotation of Stoner–Wohlfarth and localized reversal process was proposed due to the polycrystalline and imperfection of the wire. Based on H. Zeng's research [10], the corresponding coercivity could be expressed as

$$H_C = 2K_0/\mu_0 M_s - \alpha^2 \Delta K^2/(2A\mu_0 M_s) = \mu_0 M_s/2 - \alpha^2 \Delta K^2/(2A\mu_0 M_s),$$

in which A denotes the exchange stiffness, K_0 is effective uniaxial anisotropy, α determines the defect's volume and ΔK is inhomogenity accompanied by an easy-axis misalignment. From this formula one can see that high H_c can be obtained at high M_s. H_c value is about 20–30% of H_A (anisotropy field, $H_A = 2K_U/M_s$), as Sellmyer pointed out. In the case of Fe_xCo_{1-x}, M_s is about 1.5–2.0 T, so the H_c is estimated to be about 1800–3800 Oe, which is well confirmed by our experimental results. From this point, we suggest that localized reversal model is very appropriate to explain the reversal process in our Fe_xCo_{1-x} nanowires.

To summarize, we have investigated the magnetic properties of Fe_xCo_{1-x} nanowire arrays influenced on Fe component and annealing. The values of coercivity are found to increase roughly with Fe component and decrease slowly at higher Fe component peak position $x = 0.2$. Annealing effects cause the coercivity increase of Fe_xCo_{1-x} nanowires and is found not to deteriorate their squareness when the annealing temperature was low. Microstructure change during annealing process is proposed to explain the magnetic properties change of samples. In addition, The model of localized reversal model is proved to be suitable to describe our nanowires.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 60171004). The authors would like to express their appreciation to Mr. Nigel Mellors for revising this paper more carefully.

References

[1] S. Yamamoto, Y. Nakamura, S. Iwasaki, IEEE Trans. Magn. 23 (1987) 2070.
[2] S. Manalis, K. Babcock, J. Massie, V. Elings, M. Dugas, Appl. Phys. Lett. 66 (1995) 2585.
[3] R.L. White, R.M.H. New, R.F.W. Pease, IEEE Trans. Magn. 33 (1997) 990.
[4] M. Sun, Giovanni, M. Shamsuzzoha, R.M. Metzger, Appl. Phys. Lett. 78 (2001) 2964.
[5] S.Y. Chou, M.S. Wei, P.R. Krauss, P.B. Fischer, J. Appl. Phys. 76 (1994) 6673.
[6] S.Y. Chou, IEEE Trans. Magn. 85 (1997) 652.
[7] D. Routketvitch, A.A. Tager, et al., IEEE Trans. Electron. Dev. 43 (1996) 1646.
[8] X. Mei, D. Kim, H.E. Ruda, Appl. Phys. Lett. 81 (2002) 361.
[9] Y. Peng, H.L. Zhang, S.L. Pan, H.L. Li, J. Appl. Phys. 87 (2000) 7405.
[10] H. Zeng, M. Zheng, R. Skomski, D.J. Sellmyer, J. Appl. Phys. 87 (2000) 4718.
[11] K. Nielsch, R.B. Wehrspohn, J. Barthel, Appl. Phys. Lett. 79 (2001) 1360.
[12] H.R. Khan, K. Petrikowski, J. Magn. Magn. Mater. 215 (2000) 526.
[13] H.R. Khan, K. Petrikowski, Mater. Sci. Eng. C 19 (2002) 345.
[14] R.M. Bozorth, Ferromagnetism. IEEE, New York, 1991.
[15] E.C. Stoner, E.P. Wohlfarth, Philos. Trans. R. Soc. A 240 (1948) 599.
[16] D.H. Qin, M. Lu, Chem. Phys. Lett. 51 (2001) 350.
[17] H. Masuda, K. Fukuda, Science 268 (1995) 1466.
[18] V. Scarani, B. Doundin, J. Philippe, J. Magn. Magn. Mater. 205 (1999) 241.
[19] R.H. Yu, S. Basu, L. Ren, et al., IEEE Trans. Magn. 36 (2000) 3388.
[20] A. Fert, L. Piraux, J. Magn. Magn. Mater. 200 (1999) 338.
[21] G.T.A. Huysmans, J.C. Lodder, J. Appl. Phys. 64 (1988) 2016.
[22] R. Skomski, H. Zeng, D.J. Sellmyer, J. Magn. Magn. Mater. 249 (2002) 175.