Trans. Nonferrous Met. Soc. China 19(2009) s83−s87

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

Electrodeposited Ni, Fe, Co and Cu single and multilayer nanowire arrays on anodic aluminum oxide template

Bobomurod HAMRAKULOV[1], In-Soo KIM[1], M. G. LEE[1], B. H. PARK[2]

1. School of Advanced Materials and Systems Engineering, Kumoh National Institute of Technology, Gumi, Gyung Buk, 730-701, Korea;

2. Smart Applications Co. LTD, Cheonan, Chungnam, 330-814, Korea

Received 2 March 2009; accepted 30 May 2009

Abstract: The Ni, Fe, Co and Cu single and multilayer nanowire arrays to make perpendicular magnetic recording media were fabricated with nanoporous anodic aluminum oxide (AAO) templates from Watt solution and additives by the DC electrodeposition. The results show that the diameters of Ni, Fe, Co and Cu single and multilayer nanowires in AAO templates are 40−80 nm and the lengths are about 30 μm with the aspect ratio of 350−750. The magnetic properties of the prepared nanowires are different under different electrodepositing conditions. The remanences (B_r) of Ni/Cu/Fe multilayer nanowires are lower than those of others multilayer nanowires, and coercivity (H_c) of Ni/Cu/Fe multilayer nanowires are lower than those of others multilayer nanowires. These are compatible with the required conditions of high density magnetic media devices that should have the low coercivity to easily success magnetization and high remanence to keep magnetization after removal of magnetic field.

Key words: anodic aluminum oxide (AAO); nanowire; Ni; Fe; Co; Cu; magnetic property; electrodeposition

1 Introduction

After MASUDA and FUKUDA[1] reported an ordered pore arrangement in an anodic aluminum oxide (AAO), it has been widely accepted that the AAO template is an ideal mold because it possesses many desirable characteristics, including tunable pore dimensions, good mechanical property, and good thermal stability. Moreover, especially for metal nanowires, the AAO template has been proved to be a cheap and high yield technique to produce large arrays of metals nanowires by the electrodeposition[2−5]. This oxide has ordered hexagonal cells, of which every cell contains a cylindrical pore at its center. The pore diameter, cell size and barrier layer thickness can be controlled by anodizing voltage and the depth of pore by anodizing time.

The earlier investigations indicate that the magnetic nanowire arrays filled in AAO pores. These magnetic nanowire arrays offer great potential for recording media because they can achieve a recording density of more than 15.50 Gbit/cm^2 and also beyond the projected thermal limit of 6.20 Gbit/cm^2 in continuous magnetic film[6−7].

The objective of this work is to study the use of AAO template to grow well aligned Ni, Fe, Co and Cu single and multilayer nanowires by the electrodeposition[8−10]. AAO nanoporous templates were prepared with dissimilar solutions by two-step anodizing method. The new modified equipment was used for fabrication of metals nanowire in Fig.1[11]. Highly ordered Ni, Co, Fe and Cu single and multilayer nanowire arrays stand freely on the metal substrate in AAO nanoporous templates. The ordered Ni, Fe, Co and Cu single and multilayer nanowire arrays under different electrodepositing conditions were characterized by field emission scanning electron microscope (FE-SEM) and vibrating sample magnetometer (VSM).

2 Experimental

Commercial AA 1050 Al sheet (low purity 99.8% Al alloy) with a thickness of 0.4 mm was cut into 60 mm×60 mm size. These specimens were degreased with acetone for 10 min and annealed at 550 ℃ for 3 h to stop

Corresponding author: In-Soo KIM; E-mail: iskim@kumoh.ac.kr

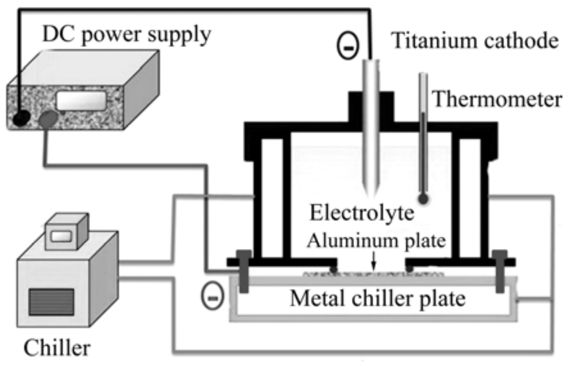

Fig.1 Equipment drawing for AAO nanotemplate fabrication [11]

the surface oxidation. Pre-treated Al samples were electropolished in a mixture of solution of phosphoric and sulfuric acids (7:2 in volumetric ratio of H_3PO_4 to H_2SO_4) to remove surface roughness and irregularities like a mirror plane. A constant current of 7.0 A was applied between the cathode and the anode for 13 min, and the solution temperature was maintained at 80−85 ℃ during electropolishing.

The specimen was used as an anode while a Ti rod was used as a cathode. A highly ordered nanoporous anodic aluminum oxide layer on the Al surface was produced by two-step anodizing method using two dissimilar solutions in equipment systems of Fig.1[11]. The first step of anodizing process was carried out in a 0.3 mol/L oxalic acid solution at 5 ℃ for 3 h. The holes interval of porous anodic alumina, in other words, the cell size, was controlled by the applied voltage in anodizing. The AAO layer was then removed by using the specimen in a mixture of 1.8% (mass fraction) chromic acid and 6% (mass fraction) phosphoric acid at 30 ℃ for 200 min. The second anodizing step continued in the same conditions (temperature and anodizing voltage) of the first step by using 10% phosphoric acid for 20 min.

Pd/Au was coated on AAO template with PVD process and then electrodeposited Cu seed layer with DC (0.5 A) for 10 min as a working cathode. After removal of aluminum and barrier layer on back side of AAO template, electroplating of nanowires was carried out at room temperature and current density of 10−20 mA/cm^2 using the same metal rods for each nanowire as an anode. Electrodeposition of nanowires was done by using the electrolytic solutions containing the following compositions: Co ($CoSO_4 \cdot 7H_2O$, 332 g/L; H_3BO_3, 30 g/L), Ni ($NiSO_4 \cdot 6H_2O$, 300 g/L; $NiCl_2 \cdot 6H_2O$, 45g/L; H_3BO_3, 45 g/L), Fe ($FeSO_4 \cdot 7H_2O$, 120 g/L; H_3BO_3, 45 g/L), and Cu ($CuSO_4 \cdot 5H_2O$, 125 g/L; H_2SO_4, 100 g/L) with saccharin as an additive. Under these experimental conditions, Co/Ni/Fe nanowires can be obtained in a wide range of elemental component ratios.

After the fabrication of nanowires, these nanowire arrays were investigated with FE-SEM and analyzed with EDS. The basic magnetic properties (coercivity, saturation field, saturation magnetic moment) were measured by a vibrating sample magnetometer (Lake Shore 7400 Series VSM System Software) after chemical removing of AAO template.

3 Results and discussion

Fig.2 shows FE-SEM images of AAO anodized in different solutions by two-step anodizing method using the 1st, oxalic acid and the 2nd, phosphoric acid with similar conditions for anodizing step. Prior to FE-SEM imaging, the alumina template was mechanically broken in Fig.2(a) and the image of cross sectional barrier layer was investigated. It can be found that these AAO nanopore images show highly ordered and uniform holes in Fig.2(b), showing that it is also possible to make anodizing of Al with two kinds of solution to prepare AAO template.

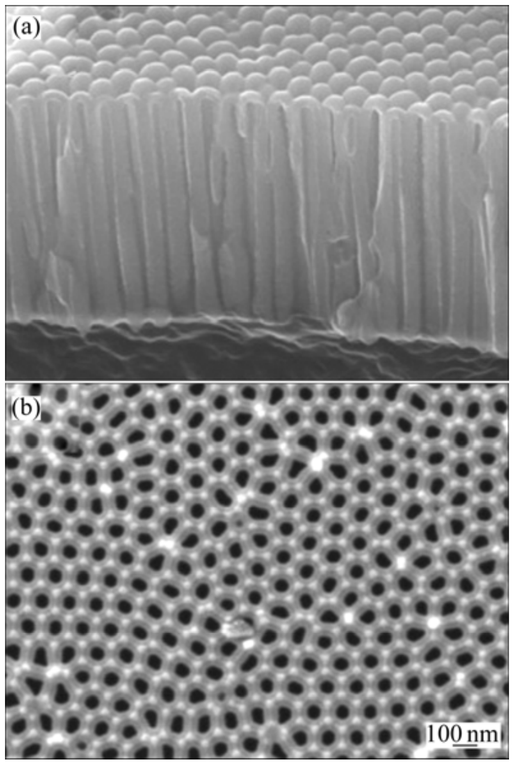

Fig.2 FE-SEM images of AAO anodized with dissimilar solutions by two-step anodizing method: (a) Cross sectional barrier layer; (b) Top view

Fig.3 shows FE-SEM images of (a) Co, (b) Ni/Cu/Fe, (c) Cu/Ni/Fe and (d) Cu/Ni single and multilayer nanowires on Cu substrate after AAO template removal. The length(L) and diameter(D)of nanowires are as follows: (a) L=730 nm, D=78 nm, λ(Co)=730 nm; (b) L=3 200 nm, D=103 nm, λ(Ni)=605 nm, λ(Cu)=1 082 nm, λ(Fe)=1 512 nm; (c) L=1 220 nm, D=93 nm, λ(Cu)=230 nm, λ(Ni)=510 nm, λ(Fe)=480 nm; (d) L=438 nm, D=90 nm, λ(Cu)=219 nm, λ(Ni)=231 nm. EDS (energy dispersive spectrometer) mapping images of metal nanowires are shown in Fig.4. The electrodeposition process can be used to fabricate a large array of uniform and continuous nanowires. The length and chemical compositions of the nanowires can be controlled by electrodeposition time and solution composition.

One of the main interesting fields in these nanowires is the magnetic properties, the saturation flux density, B_s, the coercivity, H_c, and remanence, B_r. This study is related to perpendicular magnetic recording media. The perpendicular magnetic recording media devices should have low coercivity to easily success magnetization and high remanence to keep magnetization after removal of magnetic field. The properties of coercivity and remanence of nanowires were compared with those of Co, Ni/Cu/Fe, Cu/Ni/Fe and Cu/Ni nanowires. The magnetic properties of nanowires were characterized using a vibrating sample magnetometer (VSM). The results of the VSM measurements of Co, Ni/Cu/Fe, Cu/Ni/Fe and Cu/Ni nanowires are shown in Fig.5. Fig.5 shows the saturation flux density (B_s), coercivity (H_c) and remanence (B_r) in easy (parallel to nanowires growth direction) and hard (perpendicular to nanowires growth direction) axis with different nanowire arrays: (a) B_s=4.5 μA·m^2, B_r=0.85 μA·m^2, H_c=19 586 A/m; (b) B_s=15.9 μA·m^2, B_r=1.40 μA·m^2; H_c=19 905 A/m; (c) B_s=1.1 μA·m^2, B_r=0.12 μA·m^2, H_c=19 905 A/m; (d) B_s=0.28 μA·m^2, B_r=0.041 μA·m^2, H_c=29 856 A/m. Every nanowire array shows strong anisotropy properties with the easy and hard axis. Fig.5 shows different nanowire arrays saturation flux densities, coercivities and remanence ratios. From these results, the remanences of Ni/Cu/Fe multilayer nanowires are higher than those of other multilayer nanowires, and coercivities of Ni/Cu/Fe multilayer nanowires are lower than those of other multilayer nanowires in Fig.5.

It is attributed to the GMR effect of Cu insulation metal in Ni/Cu/Fe multilayer nanowires in spintronics. Therefore, it can be concluded that these Ni/Cu/Fe multilayer nanowires are suitable for making magnetic memory devices and GMR devices.

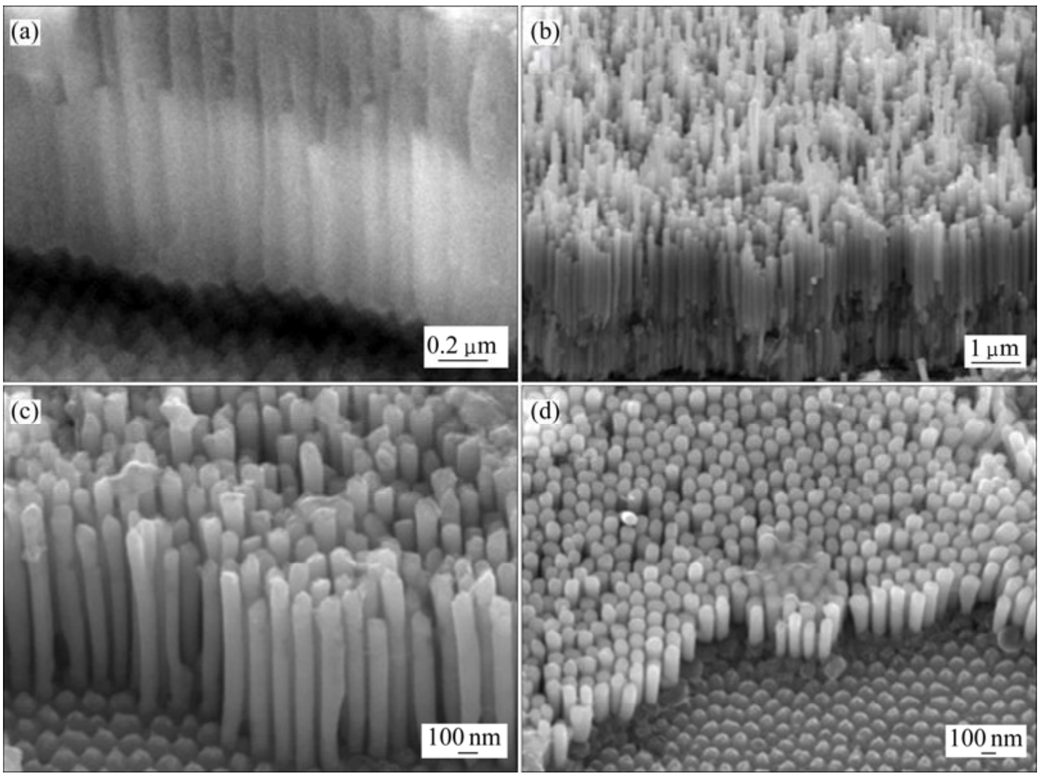

Fig.3 FE-SEM images of Co/Ni/Fe multilayer nanowires on Cu substrate after removal of AAO template: (a) Co; (b) Ni/Cu/Fe; (c) Cu/Ni/Fe; (d) Cu/Ni

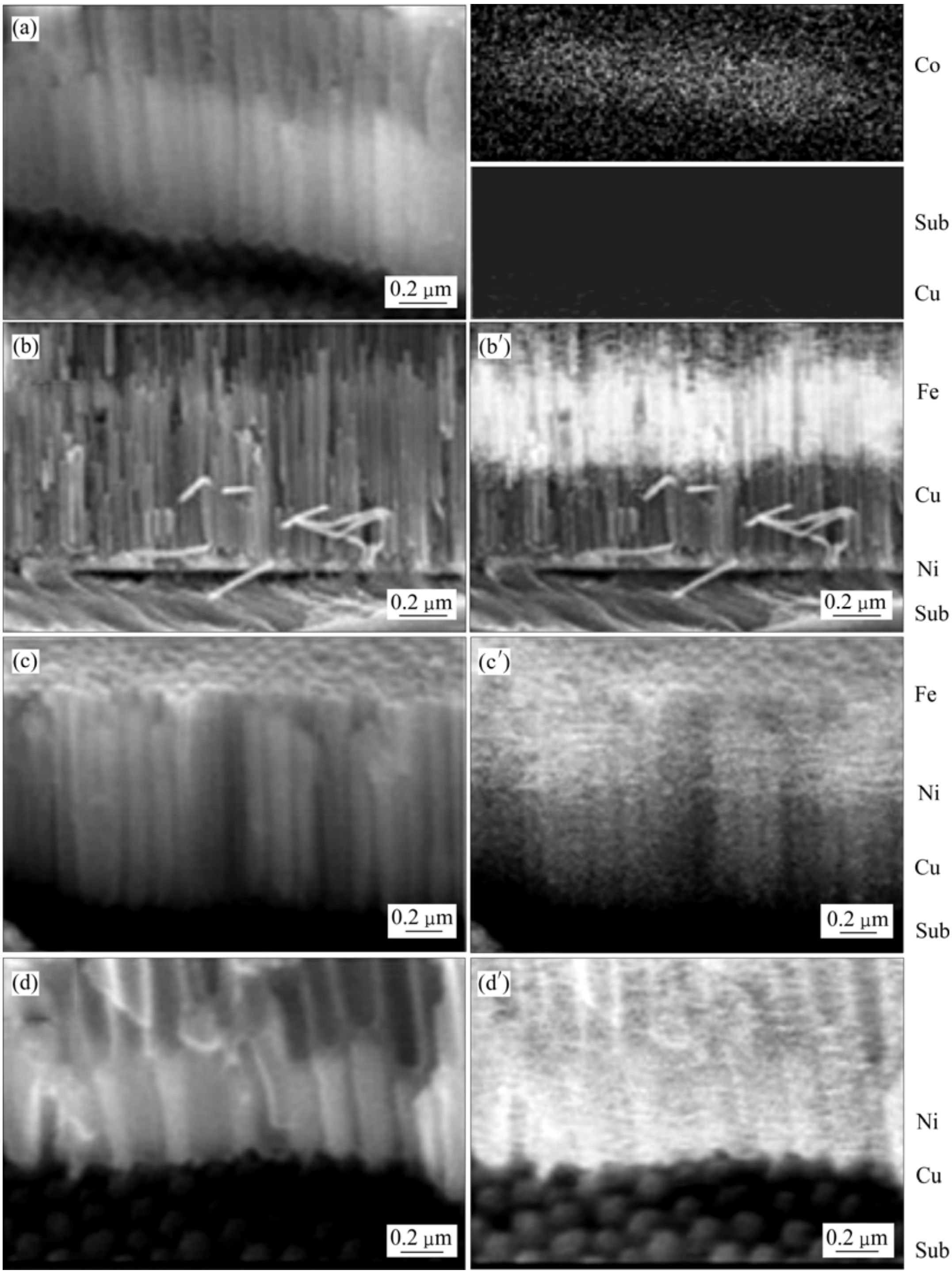

Fig.4 EDS mapping images of various nanowires: (a) Co; (b), (b′) Ni/Cu/Fe; (c), (c′) Cu/Ni/Fe; (d), (d′) Cu/Ni

4 Conclusions

1) Fabricated AAO nanopores show highly ordered and uniform holes.

2) Ni, Fe, Co and Cu single and multilayer nanowires with different lengths and diameters are electrochemically deposited on AAO pores template from sulfate electrolytes.

3) The magnetization curves of Ni, Fe, Co and Cu single and multilayer nanowires are different from the types of nanowire metals.

4) The remanences of Ni/Cu/Fe multilayer nanowires are higher than those of other multilayer nanowires, and coercivities of Ni/Cu/Fe multilayer nanowires are lower than those of others multilayer nanowires.

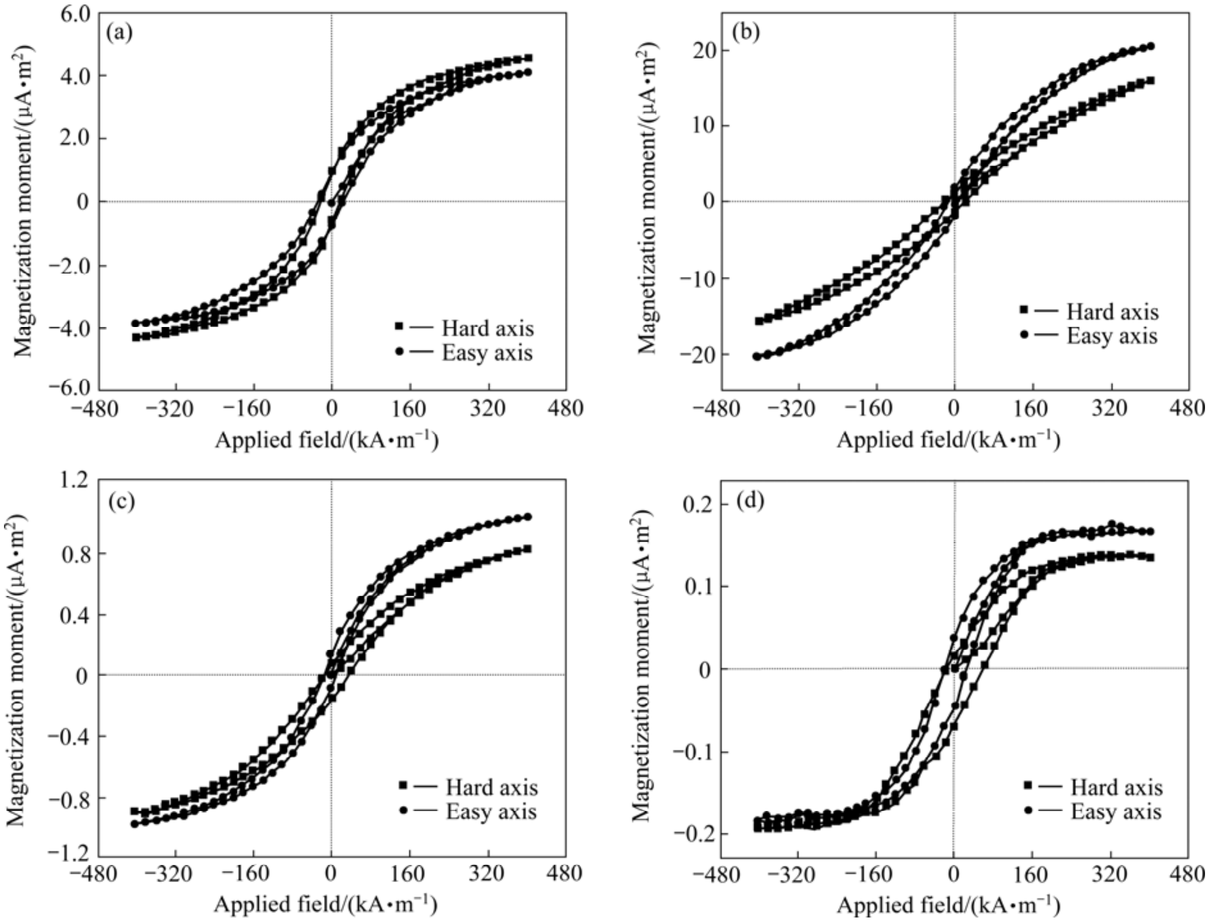

Fig.5 Hysteresis loops of single and multilayer nanowire arrays on Cu substrate: (a) Co; (b) Ni/Cu/Fe; (c) Cu/Ni/Fe; (d) Cu/Ni

References

[1] MASUDA H, FUKUDA K. Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina[J]. Science, 1995, 268: 1466−1468.

[2] SUN X, XU F, LI Z, ZHANG W. Cyclic voltametry for the fabrication of high dense silver nanowire arrays with the assistance of AAO template[J]. Mater Chem Phys, 2005, 90: 69−72.

[3] RABIN O, HERZ P R, LIN Y, AKINWANDE A, CRONIN S, DRESSELHAUS M. Formation of thick porous anodic alumina films and nanowire arrays on silicon waqfers and glass[J]. Adv Funct Mater, 2003, 13: 631−638.

[4] FEI X L, TANG S L, WANG R L, SU H L, DU Y W. Fabrication and magnetic properties of Fe-Pd nanowire arrays[J]. Solid State Communications, 2007, 141: 25−28.

[5] SAEDI A, GHORBANI M. Electrodeposition of Ni-Fe-Co alloy nanowire in modified AAO template[J]. Mater Chem Phys, 2005, 91: 417−423.

[6] ROUTKEVITCH D, TAGER A A, HARUYAMA J, ALMAWLAWI D, MOSKOVITS M, XU J M. Nonlithographic nano-wire arrays: Fabrication, physics, and device applications[J]. IEEE Trans Electron Devices, 1996, 43: 1646−1658.

[7] LU P L, CHARAP S H. Thermal instability at 10 Gbit/in^2 magnetic recording[J]. IEEE Trans Mag, 1994, 30: 4230−4232.

[8] MALKINSKIA L M, CHALASTARASA A, VOVKA A, JUNGB J S, KIMB E M, JUNC J H, Jra VENTRICE C A. Magnetoresistive multilayers deposited on the AAO membranes[J]. Journal of Magnetism and Magnetic Materials, 2005, 286: 108−112.

[9] ZHOU Ying-ke, SHEN Cheng-min, HUANG Ji-er, LI Hu-lin. Synthesis of high-ordered $LiMn_2O_4$ nanowire arrays by AAO template and its structural properties[J]. Mater Sci Eng B, 2002, 95: 77−82.

[10] LI Hua, XU Cai-ling, ZHAO Guang-yu, SU Yi-kun, XU Tao, LI Hu-lin. Fabrication and magnetic properties of amorphous Co0.71Pt0.29 nanowire arrays[J]. Solid State Communications, 2004, 132: 399−403.

[11] PARK B H, KIM I. Electrodeposited nickel nanowire array[J]. Adv Mater Research, 2007, 26/28: 585−588.

(Edited by CHEN Wei-ping)