Highly ordered magnetic multilayer Ni/Cu nanowires

R. S. Liu*1,2, S. C. Chang1, S. F. Hu2,3, and C. Y. Huang2,4

1 Department of Chemistry, National Taiwan University, Taipei 106, Taiwan
2 Taiwan Spin Research Center, National Chung Cheng University, Chia-Yi 621, Taiwan
3 National Nano Device Laboratories, Hsinchu 300, Taiwan
4 National Taiwan Normal University, Taipei 116, Taiwan

Received 5 July 2005, accepted 2 January 2006
Published online 1 February 2006

PACS 75.30.Gw, 75.50.Vv, 75.75.+a

Highly ordered nanowires with multilayer of Ni/Cu, have been successfully prepared by pulsed chemical electrodeposition into nanoporous alumina membrane. The diameter (ranging from 30 to 100 nm) of wires can be easily controlled by pore size of alumina. The applied potential and the duration of each potential square pulse determine the thickness of the metal layers. The nanowires have been characterized by transmission electron microscopy (TEM), magnetic force microscopy (MFM), and vibrating sample magnetometer (VSM) measurements. From the result of MFM analysis, the magnetic multilayer nanowire indicates unique magnetic property. The MFM images indicate that every ferromagnetic layer separated by Cu layer was present as single-domain magnet. The results are demonstrated that this type of nanowires has a potential to the application of magnetic nanodevices.

© 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction

Ferromagnetic nanowires synthesized by various methods [1–3], exhibit unique and tuneable magnetic properties due to the inherent shape anisotropy and the small wire dimensions. These nanomaterials exhibit unique magnetic properties for further application, such as high squareness and high coercivity [4]. Among various approaches to prepare nanowires, much attention has been paid to template-based synthesis in conjunction with the electrochemical deposition. It is relatively simple and inexpensive and the nanowires can be formed in a uniform and parallel porous structure. Furthermore, this method is extremely general with regard to the types of materials that can be prepared. Recently, considerable success in the preparation of nanowires arrays of metals, polymers, and so on. Many ferromagnetic nanowires of Fe, Co, Ni and their alloys are fabricated by this method. The shape and size of nanowires synthesized by template method can be confined with the pores of the template [5]. However, these nanowires often loss their high coercivity due to demagnetization by neighbouring magnetic domains. In order to overcome this drawback, the non-magnetic layer (NM) is inserted between each ferromagnetic layer (FM), to form FM/NM/FM… periodic structure. The magnetic properties of these multilayer nanowires can be varied with the thickness of FM and NM layers [6]. In this work we report the template-based synthesis of an array of Ni/Cu composite nanowires. The relationship between magnetic properties and layer thickness are discussed.

* Corresponding author: e-mail: rsliu@ntu.edu.tw, Phone: +886 2 23690152 ext.148, Fax: +886 2 23636359
2 Experimental

2.1 Preparation of anodic aluminium oxide (AAO)

In this paper anodic aluminium oxide (AAO) is chosen as template because AAO has an isolating, non-connecting, and parallel pore structure with tuneable pore diameters. The AAO membranes used in our experiments were prepared via anodic oxidation of Al foil (99%, 0.25 mm thick). Al foil was first electropolished in sulfuric acid/phosphoric acid mixed solution (H$_2$SO$_4$ : H$_3$PO$_4$ : H$_2$O = 40% : 40% : 20% in wt%) at room temperature for 10 min. After the electropolishing step, the Al foil was anodized in 0.3 M oxalic acid at 10 °C for 5–16 h to form AAO (dc current). The voltage of anodization was kept at 30 V to keep the pore size of AAO at about 30 nm. The distance between neighbouring pores is also constant. The AAO was dipped into saturated HgCl$_2$ solution to remove the remaining Al, and then dipped in 5 wt% H$_3$PO$_4$ for 3–4 h to dissolve the barrier layer. After above processes the AAO is ready for deposition.

2.2 Synthesis of Ni/Cu nanowires by electrochemical deposition

Pulsed electrochemical deposition in one bath containing both Ni$^{2+}$ and Cu$^{2+}$ ion was used for the synthesis of Ni/Cu nanowires. First a silver of 5000 Å thick was thermal evaporated onto one side of AAO to serve as back electrode. The electrochemical deposition was performed via a 3-electrode method. Pt wire is chosen to be counter electrode and the Ag/AgCl electrode is the reference electrode. The theoretical reduction potential of Ni and Cu is found to be -0.46 V (v.s. Ag/AgCl) and +0.137 V (v.s. Ag/AgCl), respectively. In order to achieve proper deposition efficiency, the reduction voltage was set at -1 V for Ni and -0.16 V for Cu. The sulfates of Ni and Cu are chosen as the sources of metal ions, and the buffer solution is 0.6 M H$_3$BO$_3$. The concentration ratio of NiSO$_4$/CuSO$_4$ is set at 100 to decrease the rate of Cu reduction during deposition of Ni. The concentration of NiSO$_4$ and CuSO$_4$ are 2 M and 0.02 M, respectively. The time of each pulse can be changed to tune the thickness of each layer. After the nanowires were formed, the silver electrode was removed by 6 M HNO$_3$, and then the AAO was dissolved by 6 M NaOH to achieve Ni/Cu nanowires. These nanowires were analyzed using TEM (H-7100, Hitachi) and X-ray diffraction (BL17A, NSRRC, Taiwan) to obtain the morphology and composition. VSM (EV5 VSM, ADE Technologies) and MFM (D3100, Digital Instrument) were used to characterize the magnetic properties of these nanowires.

3 Discussion

3.1 Morphology of Ni/Cu nanowires

Figure 1 shows the TEM micrograph of bamboo-like structure of Ni/Cu nanowires. From the figure the thickness of Ni layer and Cu layer are 400 nm and 50 nm, respectively. The existence of this structure confirms that the Ni/Cu multilayer nanowires were successfully synthesized. The diameter of nanowires is 40 nm, slightly larger than the nanowires inside the AAO (~35 nm). It is because the surface of nanowires was slightly oxidized by NaOH during the process. From the X-ray diffraction pattern of AAO deposited with Ni/Cu, we can easily find the diffraction peaks of Ni and Cu. By using the Sherrer equation to calculate the grain size of Ni and Cu, the grain sizes were found to be 36 nm and 34 nm, respectively. These values are close to the diameter of nanowires.

3.2 Magnetic properties of Ni/Cu nanowires

The lift-mode MFM phase shift graphs of Ni/Cu nanowires is shown in Fig. 2. The deposition time of Ni and Cu are 20 s (~400 nm) and 30 s (~50 nm), respectively. In the phase shift graph the difference of the brightness represents the difference of magnetic moment. Shown on the bottom right of Fig. 2 is the presentation how the magnetic tips of MFM detect the magnetic signal. The black arrows represent the direction of magnetic field. When tip moves to position 1, the magnetic field produced by Ni segment
within Ni/Cu nanowires is parallel to the direction of magnetization of tip. The phase shift image shows a “dark” region. When tip moves to position 2, the magnetic field is antiparallel, shows a “bright” region. The period length of bright to dark is the size of magnetic domain. However, the synthesized Ni/Cu wires are polycrystalline. The appearance of a single isolated domain like structure in our MFM image which may indicate that the magnetic moments in the small single crystals of polycrystalline structure are nearly arranged in the same direction. High resolution MFM may be needed to prove this assumption. Furthermore, the direction of magnetic moment is parallel to the nanowires. This result is consistent with what Guo et al. [7] found. However they did not see the bamboo-like structure in MFM graphs. This might be due to the difference of thickness of Cu. From Guo’s experiment, the thickness of Cu was only 8 nm, but in our case was 50 nm. The difference causes the magnetic moment of each Ni layer in Guo’s research merged, but was totally separated in our case. 

Fig. 3 shows the hysteresis loop of 35 nm Ni/Cu wires with different deposition time of Ni. The coercivity increases with the deposition time when magnetic field parallel to the nanowires, but remain unchanged when magnetic field perpendicular to the nanowires. This is because of the shape anisotropy of the Ni layer. In the sample which deposition time is 20 seconds (~400 nm thick), the coercivity is 895 Oe, higher than what Whitney et al. [8] reported and pristine Ni nanowires with the same diameter. This is because that in Ni nanowires each magnetic domain was connected by each other, and aligned antiparalleled. This caused the demagnetization of total magnetic moments.

Fig. 1 TEM micrograph of a bundle of Ni/Cu nanowires with diameter of 40 nm, the inset shows the bamboo-like structure.

Fig. 2 Lift-mode MFM graphs of Ni/Cu nanowires, the deposition time of Ni and Cu are 20 s (~400 nm) and 30 s (~50 nm), respectively. Black arrow represents the direction of magnetic field.
Fig. 3 Hysteresis loops of 35 nm Ni/Cu wires with different deposition time of Ni and constant deposition time of Cu (~ 50 nm). The applied fields are (a) perpendicular to the nanowires, (b) parallel to the nanowires, respectively.

4 Conclusion

We have successfully synthesized Ni/Cu composite nanowires. Each Ni layer represents a single separated domain like structure with same direction of magnetic moment. This caused the unique high coercivity and squareness, which are beneficial for future application of magnetic storage. The coercivity will become stronger with increasing Ni layer thickness due to the shape anisotropy increment. This phenomenon might be useful for the assembly of future nanodevices.

Acknowledgements This work was supported by the National Science Council of Taiwan under grant number NSC 93-2113-M-002-006 and the Ministry of Economic Affairs of Taiwan under the grant number 93-EC-17-A-01-S1-026.

References