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Journal of Magnetism and Magnetic Materials 282 (2004) 28-31

www.elsevier.com/locate/jmmm

Fabrication and magnetic properties of nickel nanowires

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Available online 15 June 2004

Abstract

By a combined technique of anodic anodization and direct current (DC) electrodeposition, we have successfully synthesized nickel nanowires by using an ordered porous alumina film as a template. In the article, the Ni nanowires with different diameter and coercivity have been found. Moreover, the Ni nanowires exhibit high perpendicular anisotropy.

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PACS: 75.30.Gw; 75.75.+a; 81.07.Vb

Keywords: Magnetic anisotropy; Anodic anodization; Porous alumina film; Electrodeposition; Ni nanowires; Hysteresis curve; Coercivity

1. Introduction

The preparation and the magnetic properties of metal nanowires electrodeposited in alumina templates have been investigated for a long time. Metal nanowires are very important both for basic research and for their potential applications in high-density recording media [1–4] and optical label [5]. They can also be considered as model systems to investigate the interaction process in one-dimensional magnetic structures [6]. In the

present paper, we use a combined technique of anodic anodization and direct current (DC) electrodeposition and have successfully synthesized Ni nanowires in the porous alumina film. The structure and magnetic properties were also investigated.

2. Experimental procedures

High-purity aluminum foils were used as substrate to synthesize porous alumina films which were taken as the template to deposit nickel metal into its nanopores. Prior to anodizing, the aluminum foils were annealed under nitrogen

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 $^{0304\}text{-}8853/\$$ - see front matter @ 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.jmmm.2004.05.023

atmosphere at 500 °C for 2 h in order to enhance the grain size in the metal and to obtain homogeneous conditions for pore growth over large area. Then, the foils were ultrasonically cleaned in isopropanol for 10 min to remove the grease that existed on the surface. Subsequently, the aluminum foils were electropolished in a 4:4:2 weight mixture of H_3PO_4 , H_2SO_4 and H_2O , respectively, for 10 min to obtain a smooth surface.

The aluminum foils were then treated in a twostep anodization process to obtain porous alumina films. The foils were first anodized under a constant voltage 30 V in a 0.3 M H₂C₂O₄ solution at 10 °C for 30 min. The formed alumina was then removed by 5 wt% NaOH at 25 °C for 2 min, and the Al sheet was reanodized under the same condition as the first step for 12 h. After anodizing, the back side aluminum was removed in saturated HgCl₂ solution for 1–2 h. A subsequent etching treatment was achieved in a 5 wt% H₃PO₄ solution to remove the barrier layer on the bottom side of alumina film. Prior to the Ni electrodeposition, a conductive layer of Au was deposited on one side of the through-hole alumina film by vacuum evaporation to serve as working electrode, and stainless steel was selected to be the counter electrode. The Ni nanowires were electrodeposited under a constant current in a mixture of 200 g/l $NiCl_2 \cdot H_2O$, 120 g/l $NiSO_4 \cdot 7H_2O$ and 50 g/lH₃BO₄ at 25 °C, and the pH was adjusted to 4 by adding NaOH solution. The Ni nanowires were liberated from the alumina template by dissolving in 5 wt% NaOH. The morphology of the alumina films and the Ni nanowires was investigated by a field emission scanning electron microscope (SEM, Hitachi S-4000) and a transmission electron microscope (TEM; Hitachi H-7100). The magnetization curves of Ni nanowires were measured by superconducting quantum interference device magnetometer (SQUID; Quantum Design MPMS7).

3. Results and discussion

In Fig. 1 we show the SEM morphology of the as-prepared porous alumina film. The porous alumina film was synthesized at a constant voltage



Fig. 1. SEM image of the as-prepared porous alumina film.



Fig. 2. SEM micrograph of the Ni nanowires.

of 30 V, and the average pore size was 30 nm. From this figure, we can easily realize the pore arrangement and the pore diameters of the porous alumina films. The SEM micrograph of the Ni nanowires which were synthesized by DC electrodeposition is shown in Fig. 2. After removing the upper part of porous alumina film, individual Ni nanowires with a diameter of 30 nm were observed. The Ni nanowires synthesized in the porous alumina film show as well the ordered arrangement as the porous alumina film prepared.



Fig. 3. TEM images of: (a) a bundle of nanowires and (b) a single nanowire (c) electron diffraction pattern of the Ni nanowire. The crystal of the single Ni nanowire is indicated by white arrow.

Fig. 3 exhibits typical TEM images of the Ni nanowires and the corresponding electron diffraction (ED) pattern. The TEM photographs of a bundle of nanowires and a single nanowire are presented in Figs. 3a and b, respectively; one can see that the Ni nanowire is long and continuous, and a bundle of nanowires resulted from incomplete dissolving. The diameter of the Ni nanowires is about 30 nm, which corresponds to the diameter of the pores in the alumina film. Moreover, it is very interesting that the Ni nanowire is formed by single crystalline Ni cylinders packing along the long axis of the wire. It reveals that the Ni nanowire exhibits a polycrystalline bamboo-like structure. The crystal (indicated by white arrow) size is consistent with the diameter of the porous alumina film. The ED pattern of the Ni nanowire is shown in Fig. 3c. The pattern is composed of several diffraction rings, indicating the polycrystalline property and the FCC crystalline structure of the Ni nanowire.

The hysteresis curves of the Ni nanowires with diameters of 30, 50 and 200 nm that were prepared by adjusting experimental parameters are shown in Fig. 4. The Ni nanowires are measured under a field applied perpendicular to the alumina film surface, and the coercivities of the Ni nanowires are 72 Oe (200 nm), 273 Oe (50 nm), and 378 Oe



Fig. 4. Hysteresis curves of the Ni nanowires with diameters of 30, 50 and 200 nm at 5 K under a field applied perpendicular to the alumina film surface. The coercivity of the Ni nanowires increases with decreasing wire diameter.



Fig. 5. Ni nanowires measured under applied field either parallel (H_{\parallel}) or perpendicular (H_{\perp}) to the surface at 300 K. The squareness of the Ni nanowires is greater when the applied field is perpendicular (S_{\perp}) to the surface than parallel (S_{\parallel}) to it.

(30 nm), respectively. It is clear that the coercivity of the Ni nanowires increases with decreasing wire diameter. This should be attributed to the tendency toward single domain nature [7]. The results of the Ni nanowires measured under the applied field either parallel (H_{\parallel}) or perpendicular (H_{\perp}) to the surface are presented in Fig. 5. The squareness (remanent magnetization/saturated magnetization) of the hysteresis curve is greater when the applied field is perpendicular (S_{\perp}) to the surface than parallel (S_{\parallel}) to it, the squareness is 0.16 (S_{\perp}) and 0.05 (S_{\parallel}), respectively. The shape anisotropy of ferromagnetic nanowires can be responsible for high magnetic anisotropy perpendicular to the substrates [8]. In general, magnetic materials with rod-like shape will exhibit a higher demagnetization field along the long axis than along the short axis. In consequence, when the external magnetic field is removed, the remanent magnetization measured along the long axis is greater than which measured in the short axis and higher squareness is acquired along the long axis.

In summary, we have successfully synthesized Ni nanowires by a combined technique of anodic anodization and DC electrodeposition. The structure of the Ni nanowires is observed by TEM and is also characterized by ED pattern to be polycrystalline. The one-dimensional nanowire is composed of several single crystals and is formed by packing of the single crystals. The magnetic properties of the Ni nanowires are investigated by SQUID, showing high perpendicular anisotropy and the relationship between the nanowire diameter and the coercivity. This template-directed synthetic method is a simple, inexpensive and versatile strategy for the fabrication of metal, semiconductor and alloy nanowires.

Acknowledgments

We thank the financial supports form the National Science Council of Taiwan under the grant number 92-2113-M-002-036 and the Ministry Economic Affairs of Taiwan under the grand number 92-EC-17-A-08-S1-0006.

References

- [1] S.Y. Chou, et al., J. Vac. Sci. Technol. B 15 (1997) 2897.
- [2] L. Wang, et al., Thin Solid Film 288 (1996) 86.
- [3] S. Dubois, et al., Appl. Phys. Lett. 70 (1997) 396.
- [4] Y.G. Guo, et al., Chem. Mater. 15 (2003) 664.
- [5] S.R. Nicewarner-Peña, et al., Science 294 (2001) 137.
- [6] R. Hertel, J. Appl. Phys. 90 (2001) 5752.
- [7] T.M. Whitney, et al., Science 261 (1993) 1316.
- [8] S.Z. Chu, et al., Chem. Mater. 14 (2002) 4595.