Journal of Alloys and Compounds 534 (2012) 6–8

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Magnetic properties of TiO_2/Ni hybrid nanotube arrays by electrophoretic deposition

Limin Guo, Xiaohui Wang *, Caifu Zhong, Longtu Li *

State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

ARTICLE INFO

Article history:
Received 25 March 2012
Received in revised form 17 April 2012
Accepted 22 April 2012
Available online 30 April 2012

Keywords:
TiO_2/Ni nanotubes
Electro-deposition
Magnetization

ABSTRACT

Magnetic Ni nanotubes (NTs) were fabricated in the pores of the self-aligned TiO_2 NT arrays by direct current electro-deposition. Crystal structure and morphologies of the TiO_2/Ni hybrid NT arrays were characterized by XRD, TEM, and SEM. The results indicated that the Ni NTs have no preferred orientation and were polycrystalline structure. Room-temperature magnetic property of the NTs was studied. The magnetic easy axis was parallel to the nanotube's channel axis attributing to the large shape anisotropy. Temperature dependent magnetization showed that the thermal energy decreasing caused an increase in coercivity by the enhanced magnetocrystalline anisotropy and dipolar interactions between NTs at lower temperatures.

1. Introduction

In recent years, much attention has been focused on the study of regular arrays of magnetic metals with dimensions in the nanometer range, such as nanoparticles, nanowires (NWs), nanotubes (NTs), or nanobelts, etc. Their potential applications in nonvolatile magnetic memory devices or high-resolution magnetic field sensors have been widely studied [1,2]. Moreover, magnetic metals with one-dimensional nanostructures as well as obvious magneto-anisotropy are good candidates for high-density magnetic recording media [3]. Various techniques are employed for the fabrication of magnetic NTs/NWs like hydrothermal method, electro-spinning or chemical techniques, etc. [3–6]. A more straightforward approach is the template technique in which the NTs/NWs are grown into pores of a template generally of a porous alumina. It is proved to be simple, cost-effective, and could precisely control the length, diameter, and composition of the NTs/NWs [7,8]. Although various magnetic metal or oxide NTs, such as Fe, Co, Ni, Fe_2O_3 or Co_3O_4 NTs, have been fabricated in the anodic alumina oxide (AAO) membranes by electro-deposition [9–11], limited information is available regarding the magnetic metal NTs grown into TiO_2 nanoporous arrays. These TiO_2/M (M = magnetic metal, oxide or composition) hybrid NT layers may be significant for exploring nano-scaled multiferroic materials (such as $BaTiO_3$/M, $PbTiO_3$/M) after a simple hydrothermal reaction for the TiO_2 template [12,13]. Strain-mediated indirect magnetoelectric coupling could arise in these separate but intimately connected phases [14].

In this paper, TiO_2 nanoporous arrays were prepared by anodization of Ti foils. Ni NTs were electrodeposited into the self-aligned TiO_2 membranes. Structure and morphologies of the hybrid NT arrays were characterized. And the influence of geometric shape and temperature on the magnetic properties of the samples was discussed.

2. Experiments

In a typical procedure, highly ordered TiO_2 NT arrays were prepared by anodization from the 99.9% purity Ti foil as described elsewhere in detail [13]. The remained Ti foils under the TiO_2 templates serves as the working electrode. The precursor electrolytes for depositing Ni NTs contained a mixture of 100 g L^{-1} $NiSO_4{\cdot}6H_2O$, 30 g L^{-1} $NiCl_2{\cdot}6H_2O$. The pH value of the solutions was adjusted with 1 M H_3BO_3 until the hydrolysate in the solutions disappeared completely. Electrodeposition process was carried out at room temperature using a two-electrode system with a platinum foil as anode. The deposition current density maintained at 1 mA/cm^2 for 3 h during the process. Then the samples were cleaned in ethanol and DI water.

Crystal structures of the specimens were determined by X-ray diffraction (XRD 2500, Rigaku, Tokyo, Japan). Microstructures of the NTs were observed by a field emission scanning electron microscope (FE–SEM, LEO-1530, LEO, Oberkochen, Germany) and a transmission electron microscope (TEM, JEOL-2010, Japan). For TEM observations, the hybrid NT layers were dispersed in acetone in an ultrasonic bath, and then carefully rinsed out with deionized water for several times. Magnetic characterization of the samples in the configurations parallel and perpendicular to the NTs axis was carried out by a vibrating sample magnetometer (VSM, 730T, Lake Shore, America). All the samples for magnetic characterizations had the same experimental conditions: sample size, temperature, etc.

3. Results and discussion

Fig. 1 shows the FE–SEM images of the as-prepared TiO_2 NT arrays (Fig. 1a) and the TiO_2/Ni hybrid NTs after electro-deposition

* Corresponding authors. Tel.: +86 010 62784579; fax: +86 010 62771160.
E-mail address: wxh@mail.tsinghua.edu.cn (X. Wang).

0925-8388/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2012.04.075

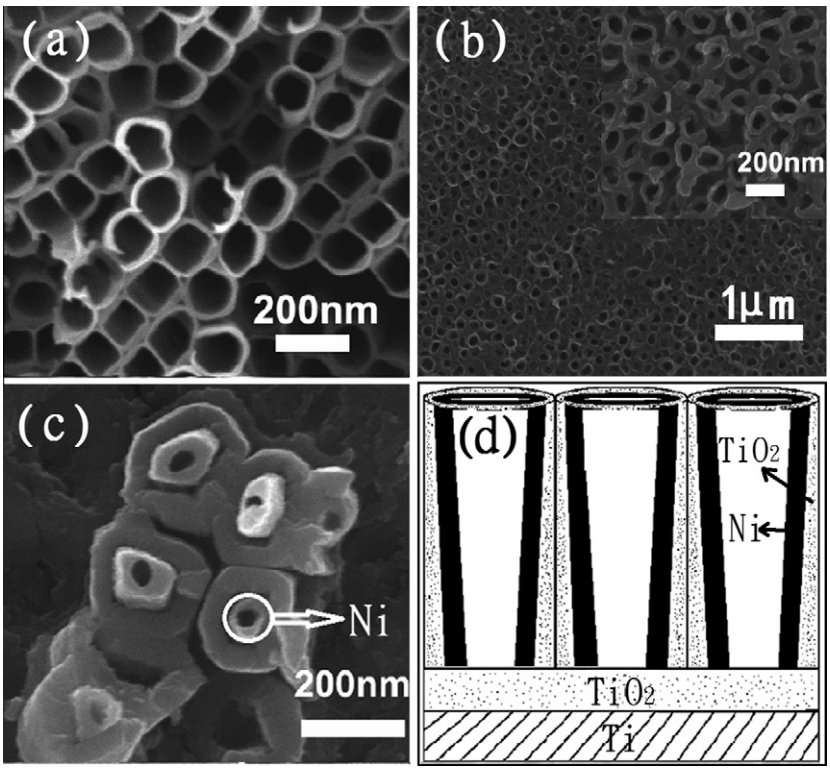

Fig. 1. FE–SEM images of TiO_2 template (a) and TiO_2/Ni hybrid NT arrays obtained under current density of 1 mA/cm^2 (b), cross-section view of b (c) and schematic illustration for the preparation of Ni NTs into TiO_2 template (d).

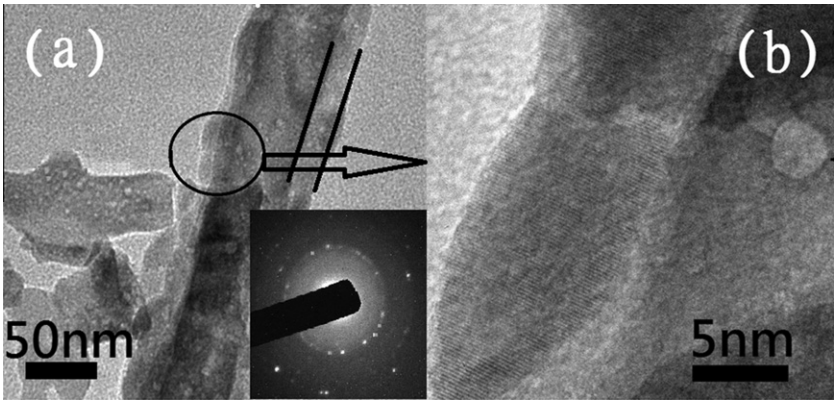

Fig. 2. TEM images of individual Ni NT (a, inset is corresponding SAED pattern) and HRTEM observation of a (b).

under current density of 1 mA/cm^2 for 3 h (Fig. 1b). The TiO_2 tubular templates have a thickness about 20 μm and an opened porous structure at the top end with diameter around 200 nm. From the top-surface views, it reveals that the outer diameters of the NTs have no distinct changes before and after deposition. But the thickness of the tubular walls has an evident increase after deposition and the uniformity of the porous layer has a little deterioration. Fig. 1c is the cross section view of the TiO_2/Ni NTs, which shows that these Ni NTs are inserted into the TiO_2 template with uniform diameters and smooth walls. The diameter of Ni NTs is corresponding to the inner diameter of TiO_2 nano-holes which demonstrates that the cations in the solution are inclined to concentrate on the pore wall of TiO_2 membranes by the driving electric field during the deposition process. Fig. 1d shows the schematic illustration of the fabricating processes for Ni nanotubes.

TEM images of the deposited Ni NT are displayed in Fig. 2, revealing that the diameter and wall thickness of the NTs is about 100 and 25 nm, respectively by deposition current of 1 mA/cm^2 for

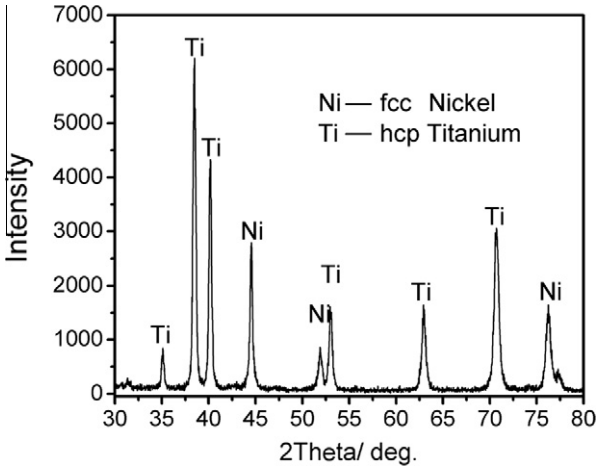

Fig. 3. XRD pattern of as-prepared TiO_2/Ni NT arrays.

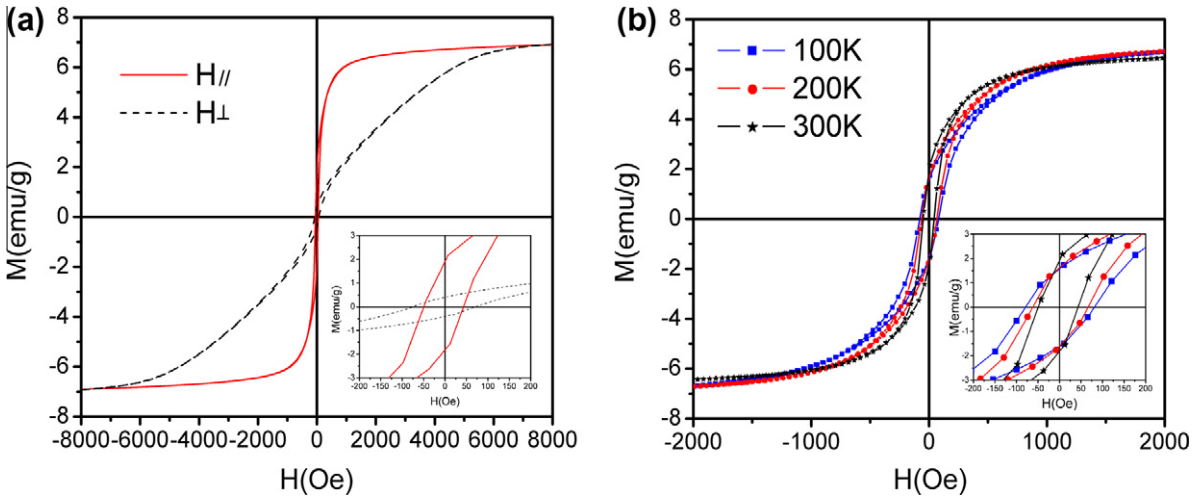

Fig. 4. M-H curves of the TiO_2/Ni hybrid NT arrays. (a): $H_{||}$, $H_{\perp}$ denote the applied field parallel and perpendicular to NT's axis respectively, (b): Measured at 100, 200 and 300 K when the applied field parallels the NT's axis.

3 h (Fig. 2a). This agrees well to the SEM results. SAED pattern of the isolated Ni NT is inserted. The weak diffuse rings doped with bright spots suggest that these Ni NTs are polycrystalline. HRTEM observation is also performed on the particles consisted in the Ni NTs. The clear lattice fringes (Fig. 2b) demonstrate that the Ni particles are well-crystallized. For further characterizing the structure of the hybrid NTs, XRD pattern of the as-prepared samples after electro-deposition is displayed in Fig. 3. Besides the Ti substrate (the anodized TiO_2 NTs are amorphous without diffraction peaks), all the other peaks agree well with those of standard face centered cubic (FCC) Ni (PDF, Card No. 4-850). The relative intensity of these peaks has no obvious difference with the criteria card, which further confirms that the deposited Ni NTs are mainly polycrystalline structure with no preferred orientation.

Magnetic hysteresis loops (M–H, Fig. 4a) of the Ni NTs embedded in the TiO_2 templates are measured at a maximum field of 10 kOe at room temperature with the external applied field parallel or perpendicular to the NTs axis. As the applied field is up to 8 kOe, the samples are saturated in both of the applied field directions and the saturated magnetization (*Ms*) value is about 6 emu/g. Moreover, the Ni NT arrays exhibit uniaxial magnetic anisotropy and the easy axis is parallel to the NTs axis. Typical coercivities are $Hc_{//} \approx 47.5$ and $Hc_{\perp} \approx 60.7$ Oe (inset of Fig. 4a), which is higher comparing to that of bulk counterparts (around 0.7 Oe for Ni) [15]. Due to the intrinsic shape anisotropy of the NTs, the parallel hysteresis yields even higher values of remanent magnetization (Mr, 2 emu/g). This is consistent with previous reports on Ni NT arrays [6,15]. Under a field applied parallel the NTs axis, the M–H curves of sample measured at 100, 200 and 300 K are shown in Fig. 4b respectively. It is observed that the shape of the curves, values of *Ms* or *Mr* have no distinct changes for the sample at different temperatures. But the *Hc* increases evidently with the reducing of temperatures because of the decrease of thermal energy at a lower temperature which weakens the shape anisotropy energy. Qualitatively speaking, the shape anisotropy is weakened by the preferential increase of the effective magnetocrystalline anisotropy as well as the dipolar interactions between the NTs at lower temperatures [11]. Further works for deeper processing of the TiO_2/Ni NT arrays, investigation of their electric or magnetoelectric coupling properties are underway.

4. Conclusions

In summary, highly ordered Ni NTs with uniform wall thickness and tube diameter have been electrodeposited into anodized TiO_2 NT arrays. All the Ni NTs show face-centered cubic polycrystalline structure. Room temperature M–H curves reveal that the easy axis of the sample parallel to the NT's channel axis attributing to the large shape anisotropy. Temperature dependent magnetization show that the coercivity of Ni NTs increases with the decreasing of temperatures because of the enhanced magnetocrystalline anisotropy as well as the dipolar interactions between the NTs under lower thermal energy.

Acknowledgments

The work was supported by Ministry of Sciences and Technology of China through National Basic Research Program of China (973 Program 2009CB623301), National Science Fund for distinguished young scholars (Grant No. 50625204), Science Fund for Creative Research Groups (Grant No. 50921061), outstanding tutors for doctoral dissertations of S and T Project in Beijing (No. YB20081000302), and Tsinghua University Initiative Scientific Research Program.

References

[1] K. Nielsch, R.B. Wehrspohn, J. Barthel, J. Kirschner, U. Gosele, S.F. Ficher, H. Kronmuller, Appl. Phys. Lett. 79 (2001) 1360.
[2] J.P. Chenga, X.B. Zhanga, G.F. Yia, Y. Yeb, M.S. Xia, J. Alloys Compd. 1–2 (2008) 5.
[3] Y.C. Sui, R. Skomski, K.D. Sorge, D.J. Sellmye, J. Appl. Phys. 95 (2004) 7151.
[4] M.A. Dar, V. Verma, V. Pandey, R. Sonkar, W.A. Siddiqui, R.K. Kotnala, Integr. Ferroelectr. 1 (2010) 135.
[5] X. Song, L. Gao, J. Am. Ceram. Soc. 91 (2008) 3465.
[6] X. Chen, K.M. Unruh, C. Ni, B. Ali, Z. Sun, Q. Lu, J. Deitzel, J.Q. Xiao, J. Phys. Chem. C 115 (2011) 373.
[7] N. Ahmad, J.Y. Chen, J. Iqbal, W.X. Wang, W.P. Zhou, X.F. Han, J. Appl. Phys. 109 (2011) 07A331.
[8] A. Saedi, M. Ghorbani, Mater. Chem. Phys. 91 (2005) 417.
[9] K.G. Kanade, D.P. Amalnerkar, H.S. Potdar, B.B. Kale, Mater. Chem. Phys. 117 (2009) 189.
[10] S. Yang, H. Zhu, D. Yu, Z. Jin, S. Tang, Y. Du, J. Magn. Magn. Mater. 222 (2000) 97.
[11] K. Pitzschel, J. Bachmann, S. Martens, et al., J. Appl. Phys. 109 (2011) 033907.
[12] Y. Yang, X. Wang, C. Sun, L. Li, J. Am. Ceram. Soc. 91 (2008) 3820.
[13] Y. Yang, X. Wang, C. Sun, L. Li, Nanotechnology 20 (2009) 055709.
[14] W. Eerenstein, N.D. Mathur, J.F. Scott, Nature 442 (2006) 759.
[15] F. Tao, M. Guan, Y. Jiang, J. Zhu, Z. Xu, Z. Xue, Adv. Mater. 18 (2006) 2161.