Characterization of electrodeposited Ni and Ni$_{80}$Fe$_{20}$ nanowires

D.C. Leitao$^a$, C.T. Sousa$^a$, J. Ventura$^a$, J.S. Amaral$^{a,b}$, F. Carpinteiro$^a$, K.R. Pirot$^c$, M. Vazquez$^c$, J.B. Sousa$^a$, J.P. Araujo$^a$

$^a$IN and IFIMUP, Institute of Nanoscience and Nanotechnology, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
$^b$CICECO, Universidade de Aveiro, Portugal
$^c$Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain

Article info
Article history:
Available online 24 October 2008

PACS:
82.45.Cc
89.75.Kd
82.45.Qr
72.15.Eb
75.75+a

Keywords:
Electrochemical properties
Conductivity

ABSTRACT
In this work we use nanoporous alumina substrates as templates for the growth of Ni and Ni$_{80}$Fe$_{20}$ nanowires. Our membranes were obtained by a two-step anodization process of high-purity aluminum foils: first anodizations were performed at 40 V for 15 h in 0.3 M oxalic acid, at 2–6°C; the second anodization was carried out using the same conditions for 30 min, resulting in pore lengths of ~1.3 μm. After the second anodization, the pore bottom barrier-layer was thinned, to allow the current to flow through electron tunneling. A pulsed electrodeposition method was then used to grow Ni and Ni$_{80}$Fe$_{20}$ nanowires. Transport characterization and isothermal magnetization measurements performed on the produced arrays are presented.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

A huge effort is being made to develop arrays of highly ordered nanostructures due to their potential application in a wide range of areas, as semiconductors, magneto-optics, biomedical, sensor devices or magnetic storing [1–3]. Nanopatterned media, and in particular arrays of magnetic nanowires, have gained increasing attention, as they offer the prospect of application as magnetic recording media. However, to achieve the desired submicron features, expensive, time consuming lithographic techniques, like e-beam or focused ion beam lithographies are usually required. An alternative route to obtain nanowires is the use of easily fabricated nanoporous alumina as templates for the subsequent growth of magnetic materials [4]. These templates present enormous advantages such as the possibility to build a net of aligned and ordered nanostructures and the ability to control their dimensions as desired. These controllable geometrical properties (length, diameter and distance between nanowires) can give rise to outstanding magnetic behaviors [5,6]. Previous works performed in arrays of Fe, Ni, Co and their alloys [7,8] mainly focused on magnetization studies and room temperature transport characterization [9]. In this work we used nanoporous alumina substrates with an average pore diameter of ~35 nm and separation of ~100 nm as templates for the growth of Ni and Ni$_{80}$Fe$_{20}$ nanowires. We characterize the transport properties (electrical resistance as a function of temperature and magnetoresistance) and perform magnetization measurements at room temperatures for these samples.

2. Experimental details

2.1. Nanoporous alumina membranes

For the growth of nanowires, nanoporous alumina templates, obtained by a standard two-step anodization method [10,11] of high-purity (>99.997%) aluminum foils, was employed. Prior to anodization, samples were properly cleaned and degreased. For surface improvement, samples were also electropolished at 20 V for 2 min in an ethanol (75%):perchloric acid (25%) solution. With this procedure a mirror surface was obtained, setting the necessary conditions for a well organized porous structure to be obtained. In this work, the first anodizations were performed at a constant voltage of 40 V for 15 h, with a 0.3 M oxalic acid solution (used as electrolyte) at a temperature between 2 and 6°C. The resulting porous-oxide layer was etched away and a second anodization of the aluminum, using the engraved hole structure as pre-pattern, was carried out with the same conditions as the first one. These anodization conditions resulted in nanoporous alumina substrates with an average pore diameter of approximately 35 nm and separation...
around 100 nm. The second anodization was performed only 30 min, producing pore lengths of ~1.3 μm. The thickness of the existing barrier-layer \((t_{\text{barrier}})\) at the pores bottom can be estimated to be around ~50 nm thick \((t_{\text{barrier}} \approx \alpha U, \text{where } \alpha \text{ is a constant with typical values between 1.2 and 1.4 nm/V [12], and } U \text{ is the applied potential})\). To be able to electrodeposit metallic nanowires in the nanoporous alumina templates, without having to manipulate the thin and fragile membranes, the deposition current has to flow through this oxide barrier, which therefore must be thinned down. The reduction procedure [4] gives origin to dendrites (small channels in the alumina barrier-layer) enabling the current to tunnel through the resulting ~2.5 nm thick barrier \((U_{\text{final anodization}} = 2 \text{ V})\).

2.2. Nanowires deposition

A pulsed electrodeposition [4] method was used to grow Ni and Ni80Fe20 nanowires. This method combines a constant current pulse for material deposition, followed by a constant potential pulse for both discharging the barrier-layer and repair membrane cracks. Finally, a resting time with no potential or current applied, enables the recovery of the ion concentration at the bottom of the pores. Different electrolytes were employed: a standard Watts bath \((\text{NiSO}_4 \cdot 6\text{H}_2\text{O}, \text{NiCl}_2 \cdot 6\text{H}_2\text{O} \text{ and } \text{H}_3\text{BO}_3)\) was used for Ni deposition, while for Ni80Fe20 a solution with \(\text{NiSO}_4 \cdot 7\text{H}_2\text{O}, \text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{H}_3\text{BO}_3, \text{sacarine} \text{and sodium-lauryl sulfate} \) was used. The ratio of Ni:Fe in the nanowires was confirmed by EDS to be 80:20. Deposition pulses with a current density of 38 mA/cm² were used for both Ni and Ni80Fe20. The electrodepositions were carried out at 30 °C. Different regimes can be observed in the \(U(t)\) electrodepositions curves: first dendrite filling occurs (Fig. 1; regime 1, high linear potential versus time dependence slope), then a slower linear is visible corresponding to pore filling (Fig. 1; regime 2) and when the nanowires start to come out of the pores a sudden decrease in potential and increase in noise is observed (Fig. 1; regime 3). The deposition was left in this regime for a considerable time to obtain a good filling uniformity. A large number of nanowires were then able to leave the pores making electrical contact with the outer surface easier to establish.

3. Experimental results

Electrical transport measurements, as a function of temperature \([R(T)]\) (Fig. 2), were performed with a standard two probe method. As bottom electrode was used the aluminum foil that was the start-point for anodization (the nanoporous alumina template with Ni and Ni80Fe20 filled nanotubes stood attached to the aluminum foil), and the top electrode was silver paste on the top of the nanowire arrays. With this set-up, the transport measurements were performed with the dendrite structure still at the nanowires bottom, together with a continuous alumina layer of ~2.5 nm. Metallic \(R(T)\) behavior (\(dR/dT > 0\)) was observed, leading us to conclude that these small structures (dendrites) and the small tunnel barrier did not affect our transport measurements considerably. The inset in Fig. 2 shows magnetoresistance (MR) at room temperature for Ni80Fe20 nanowires when the magnetic field is transverse to the nanowires long axis and consequently perpendicular to the electrical current. An almost linear MR versus \(H\) behavior is found, without any saturation feature, due to the high demagnetization factor of the individual nanowires. We were unable to perform similar measurements for the Ni samples possibly due to smaller \(M_r\) values. Magnetization measurements were performed with a commercial vibrating sample magnetometer (VSM) at room temperature. Fig. 3(a) and (b) shows the magnetization versus applied field behavior for both samples. In the case of Ni (Fig. 3(a)), we can observe an almost isotropic behavior. However an easy axis along the longitudinal nanowire direction (saturation field, \(\mu_0 H_{\text{Sat}} \approx 0.10 \text{T})\); coercive field, \(\mu_0 H_{\text{C}} \approx 0.046 \text{T})\) and an hard axis along nanowire axial direction \((\mu_0 H_{\text{Sat}} \approx 0.096 \text{T}; \mu_0 H_{\text{C}} \approx 0.03 \text{T})\) was identified. Notice that, according to the literature, a more anisotropic behavior would be expected for this system [6,7]. For Ni80Fe20 (Fig.3(b)) the expected longitudinal anisotropy behavior is observed. An easy axis along the nanowire axis with \(\mu_0 H_{\text{Sat}} \approx 0.098 \text{T}\) and a perpendicular hard axis with \(\mu_0 H_{\text{C}} \approx 0.073 \text{T}\) \((\mu_0 H_{\text{Sat}} \approx 0.026 \text{T})\) are observed.

For these hexagonally ordered arrays of nanowires there are three contributions for magnetic anisotropy that have to be considered [6]: self-demagnetization field of the whole sample, the form effect of each nanowire and the magnetocrystalline anisotropy. Due to the form effect (nanowires with aspect ratio of ~1.13), that overcomes all the other contributions for the magnetic anisotropy, Ni and Ni80Fe20 nanowires should be preferentially magnetized along the wire long axis, consequently producing a longitudinal anisotropy. For both cases an approximation of single-domain wire is expected for diameters less than ~50 nm [6,7,13]. While this behavior is observed in the Ni80Fe20 samples, where the hard axis
hysteresis cycle correlates reasonably with the expected single-domain nanowire (although with some hysteresis) the same is not observed for the Ni samples. In this case a difference can be noticed in the easy/hard coercive fields, and the hard axis magnetic behavior corresponds mainly to domain wall displacement, instead of the expected magnetization rotation. From previous studies, we know that the modification of the nanowires diameter and length can alter their magnetic response: a reduced squareness is observed due to the increase in dipolar interactions between nanowires [7] as they become more closely packed. However, this has only a noticeable effect in the easy axis direction, which is not the case for our work. So we attribute the almost isotropic characteristic observed in the Ni sample to its polycrystalline nature with spherical-like grains. This also leads to a not so sharp easy axis magnetic response.

4. Conclusions

In this work we perform transport measurements as a function of temperature and magnetization characterization at room temperature in Ni and Ni80Fe20 electrodeposited nanowire arrays. Even with the dendrite structures and a thin insulator barrier-layer at the bottom, both samples revealed the typical metallic $R(T)$ behavior. The Ni80Fe20 nanowire sample showed the expected longitudinal anisotropic behavior characteristic of a single-domain nanowire, corroborated by hard axis MR measurements, which pointed mainly to rotation magnetization processes. Ni nanowires, on the other hand, exhibit an almost isotropic behavior that was attributed to its polycrystalline nature with spherical-like grains. We were unable to detect magnetoresistance along Ni nanowires hard axis, which corroborates with the expected nanowire microstructure.

Acknowledgements

Work supported in part by Projects FEDER/POCTI n2-155/94 and PDCT/FP/63911/2005 from ITN. D.C.L., C.T.S. and J.S.A. are thankful to FCT for doctoral Grants SFRH/BD/25536/2005, SFRH/BD/38290/2007, SFRH/BD/17961/2004. J.P.A. also thanks the Fundacao Gulbenkian for its financial support within the “Programa Gulbenkian de Estimulo a Investigacao Cientifica”. The authors acknowledge funding from FCT through the Associated Laboratory (IN).

References