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Uniformity and homogeneity of Fe_XNi_{100-X} nanowires electrodeposited in nanoporous alumina

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ABSTRACT

Nanoporous alumina templates produced by two-step anodization technique with high purity aluminum (Al) sheets and oxalic acid electrolyte were used to synthesize Fe_XNi_{100-X} nanowires via potentiostatic and galvanostatic electrodeposition methods (continuous or pulsed). Scanning and transmission electron microscopy and energy dispersive spectroscopy techniques were used to investigate pore filling, length and atomic composition of the nanowires. The main results showed that uniformity and homogeneity along the length of the nanowires depend on the applied electrodeposition methods, and only the galvanostatic ones enable uniform length along the whole nanoporous alumina template with atomic composition close to permalloy.

1. Introduction

Fe_XNi_{100-X} are interesting magnetic alloys that have been applied in recording applications, microrelays, sensors, inductive devices, etc. [1,2]. Controlling the atomic composition of Fe_XNi_{100-X} alloy is possible to change its magnetic properties, making possible to produce soft and hard magnets. Soft magnetic materials are commonly used in the core of transformers, motors and generators due to properties as high permeability, low magnetic losses, and low coercivity, while the hard ones are commonly used as permanent magnets. In particular, the Fe_XNi_{100-X} alloy with 80 at% of Ni, named as permalloy (Py), has high magnetic permeance and low coercivity.

Fe_XNi_{100-X} alloys have been produced by sputtering, evaporation, pulsed laser deposition, molecular beam epitaxy, mechanical alloying and electrodeposition in the form of powder, thin films, nanodots and nanowires [3–7]. Much has been written about the potential application of Fe_XNi_{100-X} nanowires, especially in the area of high density magnetic data storage, where great effort has been done to apply them in a device [8–13]. From the theoretical point of view, magnetic nanowires arrays with reduced diameter and regularly spaced, perpendicular to a substrate, are the base for developing devices for data storage over 1 terabyte per inch [10,11]. Parkin and coworkers [12] developed a magnetic device named Racetrack Memory (RM) that has in its architecture arrays of Py nanowires perpendicular to a silicon substrate. Such RM device is based on the spin-transfer torque effect from polarized currents applied to the Py nanowires in order to read and write magnetic information. Besides the RM device enables a greater amount of magnetic data storage compared with the hard disks drives (HDDs) used in conventional computers, Hayashi and coworkers [13] showed that RM devices with Py nanowires also has an access time of the order of tens of nanoseconds, being much quicker than the ≈5 ms of the HDDs.

It is common sense to the researchers that the Fe_XNi_{100-X} nanowires are recognized as potential candidates for use in electronic devices, and due to this, great efforts have been done to produce them in a cheaper and reliable way. A common and cheap technique that has been used to produce Fe_XNi_{100-X} nanowires by several groups is the electrodeposition in nanoporous alumina (Al_2O_3) templates (NATs) produced by anodization. In fact, the anodization and electrodeposition processes are done under atmospheric pressure and ambient temperature, involving fewer steps then other processes using lithography, for example, which need several demanding steps such as photoresist remotion, chemical or ion beam etching, passivation, etc., and are not so efficient on producing dimensions smaller than 20 nm and high aspect ratio [10,14,15]. Electrodeposition technique is also recognized as enabling precise control of the composition and microstructure (grain size and growth orientation) of Fe_XNi_{100-X} alloys, which have strong influence on magnetic, mechanic and corrosive properties of the alloys and are correlated to pH, temperature of the electrolyte and current density during electrodeposition synthesis [16,17].

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The NATs employed to synthesize the Fe_XNi_{100-X} nanowires by electrodeposition are produced via anodization of Al. Anodization parameters, such as voltage, electrolyte and temperature can be tuned to produce NATs with long-range ordering of pores in a honeycomb-like structure (which depends also on the purity of the Al) with specific length, pore diameter and interpore distance [18]. Common working electrodes (WE) for plating are metals such as Al, Cu or Au [19–27]. Normally, the Al used as WE in the anodization process is not totally consumed and remains attached to the Al_2O_3 template, serving as WE for the filling of the pores by electrodeposition. Commercial NATs are not sold with Al on the bottom and a thin layer of Cu or Au needs to be sputtered on the bottom. Kok and coauthors [19] succeeded to produce Py nanowires with 18 ± 2 μm in length by pulsed potentiostatic electrodeposition using commercial NATs (without long-range ordering of pores) with pores diameter of ≈200 nm. Cho et al. [20] obtained Py nanowires with 30 ± 2 μm in length by galvanostatic electrodeposition, also using commercial NATs. Leitao et al. [21] grew Py nanowires with diameters of ≈35 nm and length of ≈1.3 μm by pulsed galvanostatic electrodeposition using NATs with long-range ordering of pores. Nguyen and coauthors [22] using a template with ordered pores used pulsed galvanostatic deposition to obtain the nanowires. In these works, the nanowires were obtained from different electrodeposition modes and templates. However, no detailed information is given about size uniformity and atomic composition of Fe and Ni along the length of the nanowires.

This paper aims to describe the correlation between potentiostatic and galvanostatic (pulsed or continuous) electrodeposition methods and the atomic composition along the length of Fe_XNi_{100-X} nanowires synthesized with the use of NATs with interpore distance of ≈96 nm and pore diameter of ≈76 nm, which were produced with long-range ordering of pores in a honeycomb-like structure. The electrodeposition is a cost efficient method and at the same time it is fundamental to know the "quality" of nanowires produced by this technique. The nanowires were characterized by energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2. Experimental details

2.1. Nanoporous alumina templates production

Highly ordered nanoporous Al_2O_3 templates (NATs) were produced to serve as masks for growing the nanowires. To produce NATs a high purity Al foil (Alfa Aesar, 99.997%) of 0.25 mm thick was pre-cut in samples of 1.0×5.0 cm^2, degreased in a mixture of neutral detergent and acetone via sonication, washed in distilled water and dried with nitrogen flux. To minimize defects in the NATs, related to the roughness of the Al, samples without a pre-annealing step were electropolished in 4:1 volume mixture of C_2H_5OH:$HClO_4$ kept under vigorous magnetic stirring, at T≤10 °C, and a voltage of 20 V applied for 2 min against a Pt counter-electrode, as performed in Ref. [28]. The distance between the Al (acting as working electrode) and Pt (counter-electrode) during the NATs preparation was ≈5 cm. The samples were than sequentially cleaned with distilled water, rinsed in ethanol and dried in nitrogen flux. The back surface and the edges were covered with an acid resistant paint and the samples then submitted to the two step anodization process [29]. The first and second step of the anodization were done using the same setup configuration of the electrochemical polishment, but with an electrolyte containing 0.3 M oxalic acid ($C_2H_2O_5$) prepared with distilled water (resistivity higher than 18 MΩ cm) and kept at 6 °C under a fixed applied voltage of 40 V during 1 h. At the end of the second step of anodization, to thin the Al_2O_3 barrier on the bottom of the templates, the anodic voltage was gradually reduced (electrochemical etching) to 30 V with a rate of 2 V/min and then to 5 V at 1 V/min. The anodization at 5 V was kept for 10 min to allow the equilibration between the forming and dissolution rates of the Al_2O_3 on the Al/Al_2O_3 and Al_2O_3/electrolyte interfaces [30]. The samples were washed with distilled water and dried in nitrogen flux. All NATs were immersed in 5 wt% H_3PO_4 solution, kept at temperatures ranging from 35 to 40 °C, for 24 min, in order to obtain samples with average nanoporous diameter of 76 nm [31]. The Al_2O_3 layer thickness of the produced NATs is ≈3 μm. More details related to the production method and characterizations of the NATs used in this work can be seen in Ref. [31].

2.2. Fe_xNi_{100-x} synthesis and characterization

To synthesize the nanowires by electrodeposition an EG & G potentiostat, model 362, was used with a three electrode configuration with a saturated calomel electrode (SCE) as reference and a platinum counter electrode. The WE was prepared by attaching the Al side of the NATs samples with conductive silver paste to a conductive stainless steel support. The electrodepositions were carried out using an electrolyte containing 1 M $NiSO_4$ +50 mM $FeSO_4$ +500 mM H_3BO_3 [19], which was kept under agitation with a magnetic stirrer and temperature controlled in the range between 22 and 30 °C, using potentiostatic (continuous or pulsed) and galvanostatic (continuous or pulsed) deposition modes. To adjust the pH of the electrolyte, drops of a H_2SO_4 solution were used. All solutions containing $H_2C_2O_4$, H_3PO_4, $NiSO_4$, $FeSO_4$ and H_3BO_3 were prepared with distilled and deionized water with resistivity of ≈18 MΩ cm. Before starting the electrodepositions, the WE with the NAT was kept immersed in the electrolyte at least for 15 min (under agitation with magnetic stirrer) in order to assure that the pores are filled with the deposition solution.

The microstructure and atomic composition of the synthesized Fe_XNi_{100-X} nanowires were characterized by using a SEM (JEOL, model JSM-6390LV) and a Field Emission Gun SEM (FEG-SEM – JEOL, model JSM-6701F) equipped with EDS (NORAN X-Ray Six microanalyses system), a 100 keV TEM (JEOL, model JEM-1011) and a 200 keV TEM (JEOL, model JEM-2100) equipped with EDS. The alumina template of some samples with synthesized Fe_XNi_{100-X} nanowires were partially/totally dissolved in NaOH solution prepared with distilled water. For those samples where total dissolution of the template happened, the precipitated Fe_XNi_{100-X} nanowires were removed from the NaOH solution using a magnet bar. The nanowires were washed with distilled water, kept in alcohol, and posteriorly pipetted and dropped on a stub or on a carbon grid for SEM and TEM measurements.

3. Results and discussion

Table 1 summarizes the experimental parameters used for production of the Fe_XNi_{100-X} nanowires in the NATs through continuous and pulsed potentiostatic electrodeposition mode. The samples 1–3 differ only in the electrodeposition time of 60 s, 1800 s (30 min) and 3600 s (1 h), respectively, used to investigate the growing process of the nanowires under a continuous potential of −1.2 V. The applied voltage is similar to the one used by Kok and coauthors [19] for Py nanowires grown via potentiostatic electrodeposition and using commercial NATS

Table 1
Deposition parameters for growing Fe_XNi_{100-X} nanowires by continuous and pulsed potentiostatic depositions: potential (*V*), time (*t*), pH, number of cycles (n°) and temperature (*T*).

	Experimental parameters				
Sample	***V* (V)**	***t* (s)**	**pH**	**n°**	***T* (°C)**
1	−1.2	60	3.65	–	30
2	−1.2	1800	3.65	–	30
3	−1.2	3600	3.65	–	30
4	−1.2	1	2.56	3600	23
	−0.4	1			