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DC electrodeposition of NiGa alloy nanowires in AAO template

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ABSTRACT

NiGa alloy nanowires were electrodeposited from an acidic sulfate bath into nanoporous anodized alumina oxide (AAO). This template was fabricated by two-step anodizing. The effects of bath composition and current density were explored on the Ga content of electrodeposited nanowires. The Ga content in the deposits was increased by increasing both Ga in the bath composition and electrodepositing current density. The NiGa alloy nanowires were synthesized for Ga content up to 2–4% without significant improving the magnetic properties. Above this threshold Ga clusters were formed and decreased the magnetic properties of the nanowires. For Ga content of the alloy above 30%, the wires were too short and incomplete. X-ray diffraction patterns reveal that the significant increase of Ga content in the nanowires, changes the FCC crystal structure of Ni to an amorphous phase. It also causes a sizeable increase in the Ga cluster size; these both lead to a significant reduction in the coercivity and the magnetization respectively.

1. Introduction

Metallic alloys, obtained either by electrochemical or metallurgical procedures, are important due to their many possible industrial and technological applications. The fabrication of nanowire arrays has attracted much interest recently owing to their potential use in high density perpendicular magnetic memories [1], giant magnetoresistance (GMR), sensors [2,3], and magnetoelectronic devices [4,5]. Electrodepositing of gallium is prohibitively difficult. Recently, some methods and chemistries for depositing gallium thin films were reported [6]. To the best of our knowledge co-deposition of Ni and Ga has not been reported, and it can help to overcome the challenge of the deposition of Heusler alloy Ni–Mn–Ga. Moreover, the magnetic properties of electrodeposited NiGa alloys has not been explored yet. An interesting change in magnetic behavior can be expected to occur on alloying the ferromagnetic nickel with diamagnetic gallium by electrodeposition. Any attempt to study the correlation between magnetic properties and deposition parameters could also be of immense use. Many techniques have been used to fabricate magnetic nanowires [7,8]. However, the template-assisted electrodeposition method has been shown to be one of the simplest, the most inexpensive and easily controlled methods. The porous alumina is considered as particularly attractive template materials for fabricating nanowires since it has a high pore density, a uniform pore distribution and a small pore diameter [9,10]. Metallic elements such as Fe, Co and Ni magnetic nanowires prepared by the porous alumina template possess uniaxial anisotropy with the easy axis along the wire axis, which arises from the shape anisotropy of the wires [11–14]. This effect could be interesting for the magnetic properties of the NiGa alloy nanowires. The effective plating parameters like bath composition and current density are known to change the composition of the alloy [15]. In this work, the magnetization behavior of the electrodeposited NiGa nanowires prepared from sulfate bath with different Ni/Ga ion ratio in the bath and different current density have been studied.

2. Experimental procedure

2.1. Template fabrication

To fabricate the template, highly pure aluminum foils of 0.3 mm thickness were degreased with acetone for 10 min and annealed at 450 °C for 1 h in an inert argon atmosphere to prevent any surface oxidation. Then, the specimens were electro-polished in a 1:4 volume mixture of perchloric acid and ethanol at room temperature. The foils were anodized in 0.3 M oxalic acid solution at 15 °C for 15 h with anodization voltage of 40 V. The anodized foils were immersed in a solution composed of 0.2 M chromic and 0.5 M phosphoric acid at 70 °C for 15 h to remove the anodized layer. The foils were again anodized according to the first step for 1 h. DC electrodeposition of alloy nanowires in AAO pores needs to

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remove the nonconductive barrier layer in order to get to the conductive Al surface. Barrier layer modification was accomplished at the end of second anodizing process. The voltage was first reduced to 20 V at a rate of 0.066 V s^{-1}, then to 10 V at rate of 0.033 V s^{-1}, and to 6 V at rate of 0.0165 V s^{-1} and to 3 V at rate of 0.0083 V s^{-1}. In final stage, to remove remaining barrier layer, AAO template was immersed in a 1 M phosphoric acid solution for 30 min according to [16].

2.2. Synthesis of NiGa nanowires

DC electrodepositing technique was performed in a simple electrochemical cell with two electrodes to deposit nanowires into the AAO nanopores. Different Ga contents in deposited nanowires were obtained at a constant current density (30 mA/cm^2) using different Ni/Ga ion ratios. More precisely A 0.1 M solution composed of different $NiSO_4 \cdot 6H_2O/GaSO_4 \cdot 18\ H_2O$ ratios ranging from 100/0 to 83/17 and 40 g l^{-1} $(NH_4)_2SO_4$ was used as electrolyte for nanowires electrodeposition. To study the effect of the current density a 0.1 M solution composed of 90% $NiSO_4 \cdot 6H_2O$, 10% $GaSO_4 \cdot 18H_2O$ and 40 g l^{-1} $(NH_4)_2SO_4$ was used as electrolyte. The pH value of the electrolyte solutions were initially 2.5–3, and did not change during deposition. The electrodeposition time for all samples was 180 s. Philips XL30 scanning electron microscopy (SEM) was employed to investigate the morphology of template and nanowires. The chemical composition of the nanowires was determined by Energy-Dispersive X-ray analysis (EDX). The magnetic properties were measured by a homemade alternating gradient force magnetometer (AGFM) at room temperature. The X-ray diffraction measurement, for determining crystal structure was carried out using an XPert MPD diffractometer type. XRD was performed in θ–2θ mode using Cu-Kα radiation with a wavelength of 1.5418 Å.

3. Results and discussion

The chemistry of the electrolyte system was studied using cyclic voltammetry at first. Distance between reduction potential of nickel–water and gallium–water systems as well as the effect of $(NH_4)_2SO_4$ as a decreasing agent of gallium reduction potential is shown in Fig. 1. To move the reduction potential of Ga^{+3} closer to that of Ni^{+2}, 40 g l^{-1} of $(NH_4)_2SO_4$ was used as a complex agent. This agent decreases the reduction potential of Ga and allows the electrodeposition of nickel and gallium at the same time.

Fig. 2a and b shows the SEM top view of the AAO template after the second anodization and immersion in acid phosphoric for 30 min, respectively. As illustrated in Fig. 2a, hexagonal self-assembled nanopores were formed with 40 nm diameter which as it is seen in Fig. 2b increases to about 50 nm after immersing in

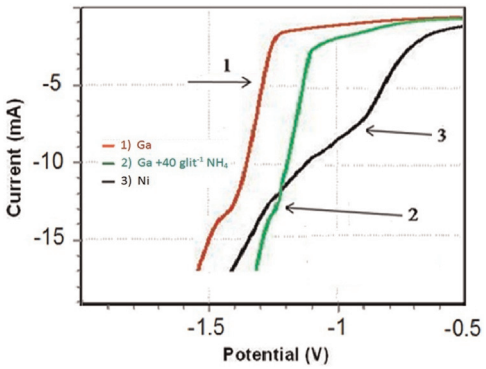

Fig. 1. Cyclic voltammetry of 0.1 M $NiSO_4$, $GaSO_4$ and $GaSO_4 + (NH_4)_2SO_4$ solutions.

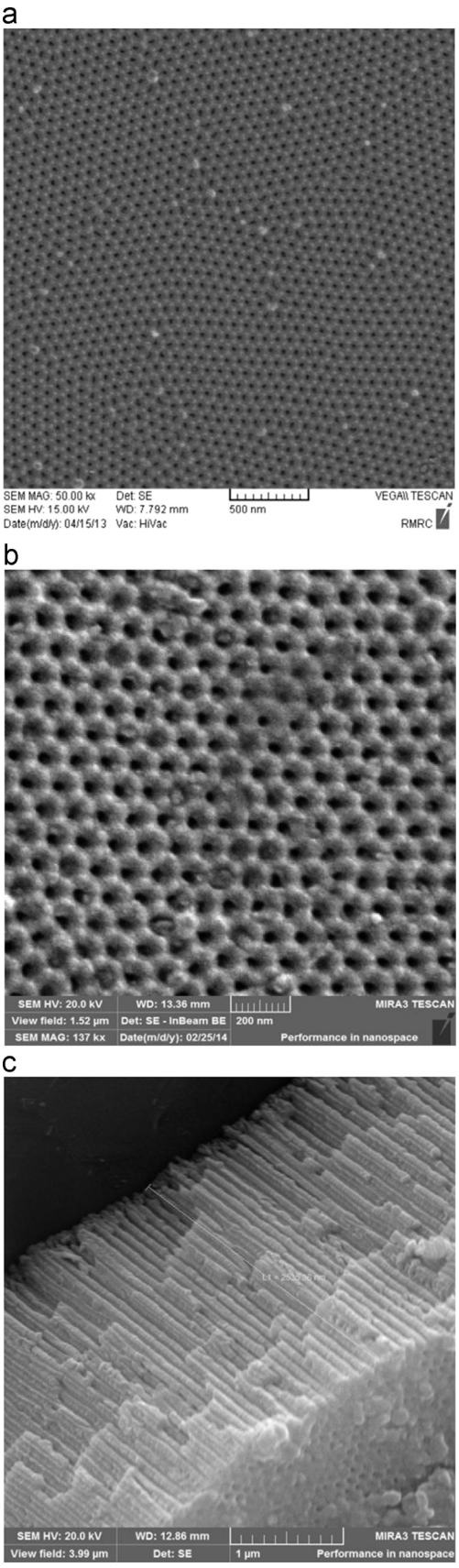

Fig. 2. (a) SEM image of AAO template after second step anodization, (b) SEM image of AAO template after 30 min immersing in phosphoric acid and (c) the cross section SEM image of AAO template.