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Preparation and magnetic properties of Co and Ni nanowire arrays

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This paper reports some results on the synthesis and magnetic properties of cobalt and nickel nanowire arrays. Cobalt and nickel nanowire arrays have been synthesised by chemical electrodeposition in a three electrode cell. The pore size of the membranes and morphology of electrodeposited nanowires were studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Magnetic characteristics of the obtained nanowire arrays were determined at room temperature by using a vibrating sample magnetometer (VSM), in an external magnetic field of 15 kOe.

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1. Introduction

In recent years much attention has been paid to the understanding of nanostructured materials (such as nanoparticles, nanowires, multilayers, etc.), which exhibit interesting magnetic properties. The miniaturization of the magnetic systems with nanometric scale dimensions makes it possible to obtain magnetic properties, which do not appear in bulk material and are of great scientific and technological interest. Electrochemical techniques, which are very simple and cheap, make possible the synthesis of objects in the nanometric scale. "Template synthesis" is an elegant chemical approach to the manufacturing of nanostructured materials, in particular for different kinds of nanowires.

The work presented here involves the production and use of anodic aluminum oxide Al_2O_3 (AAO) templates for growth of aligned nanowire arrays. Aluminum anodizing was used to create these nanoporous templates. The aluminum anodizing process is tunable with regards to both pore diameter and pore length, depending on the anodizing voltage and time, respectively. This allows the production of tailored AAO templates, leading to other potential applications, such as self-organized assemblages of quantum dots, field emitters, and other magnetic electronic, and optoelectronic devices [1, 2].

Arrays of nanowires are very attractive for their potential applications in high-density magnetic recording devices and sensors, as well as for fundamental scientific studies of nanomagnetics. The ability to produce highly ordered nanowire arrays cheap and effectively is important for both purposes.

In this paper we report some experimental results concerning the synthesis and magnetic properties of cobalt and nickel nanowires obtained by electrochemical deposition.

2. Experimental details

Aluminium is always covered with a thin oxide because of its affinity for oxygen. Aluminium oxide film can also be produced when pure aluminium is used as an anode in an electrolytic cell. This oxide film is called anodic aluminium oxide (AAO) film. In this case, there form two types of oxide films, a dense barrier film and a porous film. Type of oxide film depends on the nature of the electrolyte solution used in anodization. The thickness of barrier-type oxide film can only be controlled by anodizing voltage, whereas that of porous-type oxide film can be adjusted by the current density and anodizing time.

The formation of AAO film is affected by the anodic voltage, the temperature of electrolyte, and the first anodizing time. The anodic voltage and the temperature of electrolyte affect the growth rate of pores and the interpore distance.

A pure aluminium sheet (99.999%) of 0.25 mm thickness was degreased in acetone. This was annealed at 500 ºC under nitrogen for 5 hours to promote recrystallization and grain growth. Annealed specimen was washed with pure ethanol by ultrasonication and rinsed in deionised water. The aluminium sample was electropolished in a mixture 1:4 of perchloric acid and ethanol to remove surface irregularities. A constant voltage of 20 V from a power source was applied between the platinum cathode and aluminium sample as anode for 60-120 seconds. The electropolishing time was varied with the characteristics of the used Al specimens such as thickness and roughness. The solution temperature was kept to be 0º C during electropolishing. After electropolishing, the specimen was rinsed several times in ethanol for more than 15 min, then rinsed in deionised water and finally dried in an air stream. The sample is then put through a three-step anodizing process in a 0.3 M oxalic acid solution.

The first step anodizing was performed at 40 V, 10-25 hours, 5º C to allow the growing AAO layer with hexagonally ordered pore structures. Experimental setup was the same as what used in electropolishing, except that an oxalic acid was used instead of a perchloric acid-ethanol solution. After the first anodization was realised, AAO layer was removed by immersing the specimen in a solution of 0.2 M chromic acid and 0.4 M phosphoric acid at 65º C for 30 - 60 minutes. The surface with regular hexagonal texture formed in the first anodization acts as a mask for the second anodization process. This is performed in the same conditions as the first anodizing at 2 - 10 hours. The sample is then put through a chemical pore widening process in 0.3 M phosphoric acid at 35º C for 30 minutes to increase the diameter of the pores. To create uniform barrier thickness, a third step anodizing is performed for 4 minutes at 25 V, followed by a slow step down of the current.

The Co and Ni nanowire arrays were prepared by electrochemical deposition into obtained nanosized pores of AAO, using a typical three-electrode assembly controlled by a potentiostat PGZ 100.

For the electrodeposition a platinum piece was used as counter electrode and an Ag/AgCl electrode as reference electrode.

The growth of nanowires was performed at room temperature from solutions containing metal sulphate and chloride and boric acid. The bath composition for the electrodeposition of Ni nanowire array was: $NiCl_2 \cdot 6H_2O$ (45 g/l), $NiSO_4 \cdot 7H_2O$ (300 g/l), H_3BO_3 (45 g/l), pH 3.5. The bath composition for the electrodeposition of Co nanowire arrays was: $CoSO_4 \cdot 7H_2O$ (300 g/l) and H_3BO_3 (45 g/l), pH 4.48.

The employed current densities varied between 60 and 80 mA/cm^2.

Fig. 1 shows schematically the electrodeposition procedure for the preparation of the Co and Ni nanowire arrays.

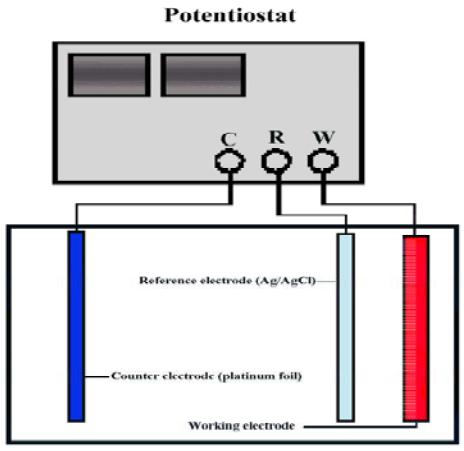

Fig. 1. Schematic setup for nanowires electrodeposition.

The morphology of obtained AAO membranes and nanowires were studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Magnetic characteristics of the Co and Ni nanowire arrays were determined at room temperature by using a vibrating sample magnetometer (VSM), in an external magnetic field of 15 kOe, applied parallel and perpendicular to the long wire axis.

3. Results and discussion

The AFM 2-d and 3-d images presented in Fig. 2 reveal the morphology of the pores in AAO membrane. We can observe that an ordered nanopore array is obtained after the second anodization if the same parameters are used as in the first anodization step.

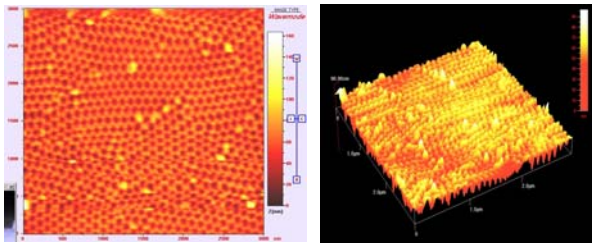

Fig. 2. AFM 2-d and 3-d images of AAO membrane.

The morphology and length of electrodeposited nanowires were studied by SEM and AFM, after the dissolution of the AAO membrane in sodium hydroxide (NaOH).

In Fig. 3 is presented a SEM micrograph of Co nanowires. It can be observed that the lengths and diameters of nanowires are uniform. The length of Co nanowires was about 5 μm and the diameters of nanowires were 80 nm.

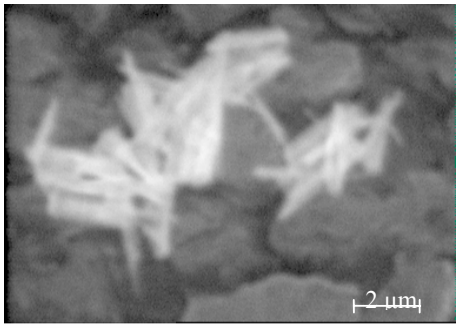

Fig. 3. SEM micrograph of Co nanowires.

Fig. 4 shows the SEM micrograph of Ni nanowires. The length of Ni nanowires was about 3 μm and the diameters of nanowires were 80 nm.

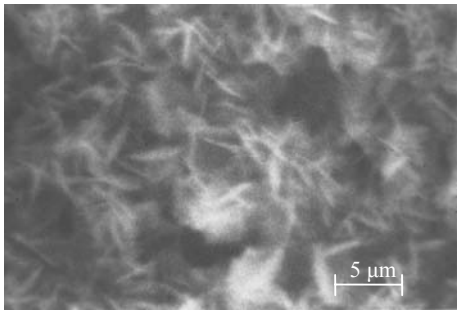

Fig. 4. SEM micrograph of Ni nanowires.

The hysteresis curves oh the Co nanowire arrays obtained in porous AAO membrane, with a diameter of about 80 nm and a length of about 5 μm are shown in Fig. 5. The coercivities of the Co nanowire arrays were 316 Oe for the applied field parallel to nanowires and 240 Oe for the applied field perpendicular to nanowires.

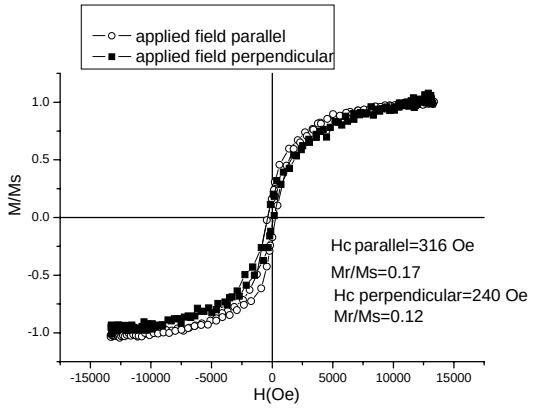

Fig. 5. Hysteresis loops for Co nanowires.

The hysteresis curves oh the Ni nanowire arrays obtained in porous AAO membrane, with a diameter of about 80 nm and a length of about 3 μm are shown in Fig. 6. The coercivities of the Ni nanowire arrays were 322 Oe for the applied field parallel to nanowires and 367 Oe for the applied field perpendicular to nanowires.

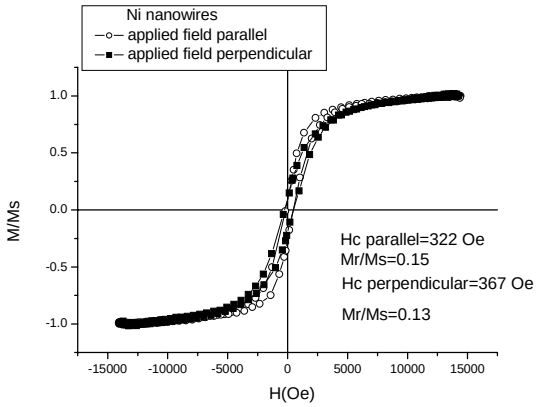

Fig. 6. Hysteresis loops for Ni nanowires.

4. Conclusions

Highly ordered pore array in anodic aluminium oxide was fabricated by anodizing pure aluminium. The order of a pore array was affected by anodizing voltage, electrolyte temperature, and first, second and third anodizing time. The measured interpore distance showed linearity with anodizing voltage. Control of pore size dispersion requires careful control of the anodization steps. By control of the parameters of electrodeposition process (time, voltage, temperature of solutions), Co and Ni nanowire arrays with soft magnetic properties were obtained.

References

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