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Template Synthesis and Composition of Bimetallic Co/Ni Nanostructures Arrays

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Nanostructures, based on nickel and cobalt, are promising for the development of magnetic metamaterials. Magnetic nanotubes have become a symbol of new and fast developing research area of nanotechnology. Their potential applications are in many fields, including electronics, catalysis, magnetism and electrochemistry. The template method is commonly used to prepare this kind of materials. The paper describes magnetic nanotubes and nanowires preparation method, based on electrochemical deposition in track etched membranes. Various electrolytes have been used to obtain nanostructures of different cobalt and nickel compositions. We have obtained the ordered arrays of bimetallic cobalt/nickel nanostructures with sizes from 70 to 600 nm.

Keywords: Track etched membrane, Template synthesis, Bimetallic nanostructures, Electrochemical deposition, Nanotube, Nanowire.

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1. INTRODUCTION

Track etched membranes (TEM) obtained by heavy ion irradiation of polymer films and etching processes have many significant applications in nanotechnology. Template synthesis of magnetic nanostructures, based on electrochemical deposition, is the one of such applications. This method allows to obtain micro-scale materials with regular structure, which are of great interest because of their potential applications in many fields, including electronics, catalysis, magnetism, and electrochemistry [1, 2]. During the last decade, properties of magnetic nanowires and nanotubes have attracted much attention. Nanostructures, based on metal deposits of alloys of cobalt with nickel, are promising for the development of new magnetic nanodevices. Recently, magnetic nanotubes have been fabricated and have become a symbol of new and fast developing research area of nanotechnology because of their technological applications in magnetic biotechnology [1-5]. Electroless deposition and electrochemical deposition are widely employed to deposit metals in templates. Electroless deposition method normally requires reducing agents and a noble metal catalyst. In the electrochemical deposition method conductive layer is needed on the one side of the membrane to use it as cathode. There are several techniques to produce conductive layer on membrane, magnetron sputtering is a one of such methodes. It has been studied that if the pores of membrane were not completely covered deposit growth tended to be tubular [3]. From theoretical point of view, tube geometry has advantages over wire geometry because it completely avoids a problem of mathematical singularity in micromagnetic distribution leading to uniform switching fields [2]. Geometrically, magnetic nanotubes are characterized by their external and internal radii R and a, respectively, height (or length) H, and thickness t ($t = R - a$), where $a = 0$ gives a solid cylinder geometry (wires) and $t > 0$ gives a hollow cylinder geometry (tubes). In this letter, we will present the experimental results regarding the obtaining of magnetic nanotubes and nanowires using various solutions.

2. EXPERIMENT

2.1 Preparation of track etched membrane template

PET film with a normal thickness of 12 and 19 microns was irradiated with 1.75 MeV/nucl Kr-ion beams with the ion fluency of $1 \cdot 10^9$ cm^{-2} and $1 \cdot 10^7$ cm^{-2} respectively at the DC-60 cyclotron in Astana. Ultraviolet (UV) sensibilisation during 30 minutes from each side was used to accelerate the etching process of irradiated material. Etching was performed in 2.2M NaOH at the temperature 85 °C. For membrane with pore density $1 \cdot 10^9$ cm^{-2} etching time was 70 sec and for membrane with pore density $1 \cdot 10^7$ cm^{-2} etching time was 5 min. These etching modes allowed us to obtain membranes with cylindrical pores. Their diameters were about 70 nm and 590 nm respectively (see Table 1).

2.2 Electrochemical deposition

Two-electrode electrochemical cell has been used for deposition of magnetic nanostructures. Electrochemical deposition was carried out in the channels of track etched membranes in potentiostatic mode. Fig.1 shows a schematic diagram of a cell used for electrochemical deposition.

Polypropylene was chosen as the base material of the cell because of its chemical stability to solutions that used in deposition process. Thin platinum plate was used as anode and was placed above the polymer template that was the cathode.

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Electrical contact was established by coating one side of the membrane with 20 nm film of gold using magnetron sputtering. After that, gold covered film was assembled into conductivity cell, and deposition of alloy of Co/Ni was carried out inside the template.

Conditions of deposition are shown in Table 1. Ascorbic acid ($C_6H_8O_6$) was added to adjust the desired pH value.

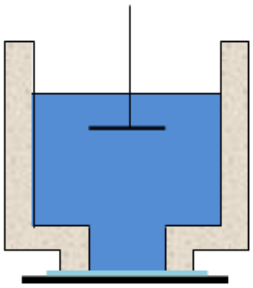


Fig. 1 – Schematic diagram of two-electrode electrochemical cell for deposition

Control of the deposition process was performed by chronoamperomety using a multimeter Agilent 34410A and special software that allows recording the experimental values to a PC.

Table 1 – Experimental conditions for obtaining bimetallic Co/Ni nanostructures

№	PET template	The composition of the electrolyte	Conditions of deposition	$\nu(Co^{2+})$ / $\nu(Ni^{2+})$
1	$1.0 \cdot 10^9$ pores/cm², thickness - 12 um, pore size - 70 nm	$CoSO_4 \cdot 7H_2O$ (120g/l), $NiSO_4 \cdot 6H_2O$ (100.14 g/l), H_3BO_3 (45 g/l), $C_6H_8O_6$ (1.5 g/l)	Voltage 1.69 V, deposition time 17.5 min	1/1.12
2	$1.0 \cdot 10^7$ pores/cm², thickness - 19 um, pore size - 590 nm	$CoSO_4 \cdot 7H_2O$ (120g/l), $NiSO_4 \cdot 6H_2O$ (100.14 g/l), H_3BO_3 (45 g/l), $C_6H_8O_6$ (1.5 g/l)	Voltage 1.69 V, deposition time 80 min	1/1.12
3		$CoSO_4 \cdot 7H_2O$ (98.38g/l), $NiSO_4 \cdot 6H_2O$ (91.89 g/l), H_3BO_3 (45 g/l), $C_6H_8O_6$ (1.5 g/l)	Voltage 1.69 V, deposition time 50 min	1/1

After the electrochemical deposition the PET templates with Co/Ni nanowires and nanotubes were immediately removed from the electrolyte, first rinse with distilled water and ethanol, finally dried in air at room temperature and subjected to further analysis.

To ensure integrity of the nanotube array, all samples were covered with massive copper substrate by electrochemical deposition. The polymer membrane was removed by dissolving it in 9M sodium hydroxide for 15 minutes at 85 ºC. Acetic acid was used to lower the pH to neutral and then samples were washing with several times with distilled water.

Elemental composition of the samples was determined from energy dispersive analysis (EDA).

3. RESULTS AND DISCUSSION

Cronoamperometry analysis for synthesis of nanostructures can accurately control the length and shape of the resulting nanowires. There are three common stages at current/time experimental curves during potentiostatic mode.

Stage 1 – start of filling of the template, the growth of the nanowires/nanotubes inside of the membrane.

Stage 2 – end of filing the template, the beginning of the deposition process on the surfacw of the membrane.

Stage 3 – the metal deposition on a solid surface.

Fig. 2 shows the experimental curve of the current change in the process of deposition of Co/Ni from the working electrolyte solution.

As seen from the graph shown in Fig. 2, the deposition process was stopped in the final third stage, when the membrane if formed of a massive cast layer. After removing the template, in scanning electron microscope micrographs were prepared ordered array of nanostructures (Fig. 3 (a, b)). The size of thread like wires does not exceed 65-75 nm.

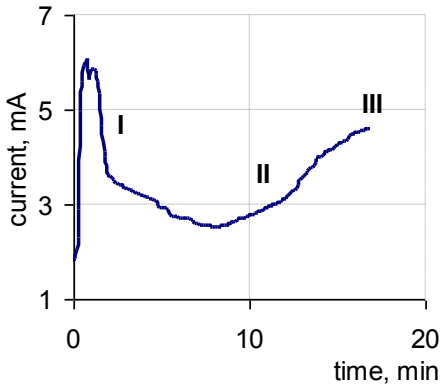
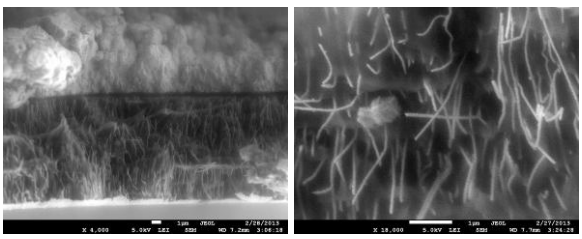


Fig. 2 – Chronoamperogramm of the electrochemical deposition of Co/Ni in the channels of track etched membrane with pore size 70 nm

In case of the second type of PET template, electrolytes with various Co/Ni ratios were used to obtain the nanotubes with different metals ratio (see Table 1).

Typical chronoamperogramms of deposition process for each of the electrolyte compositions used are shown in Fig. 4. In this case, in contrast to the graph shown in Fig. 2, the deposition process was interrupted at the stage of 1-2, i.e. the height of nanotubes does not exceed the thickness of the polymer template. The "trial" experience was carried before obtaining such samples. The time required until the beginning of phase 3 is



a b

Fig. 3 – Highly ordered arrays of nanowires after template removing (a, b)

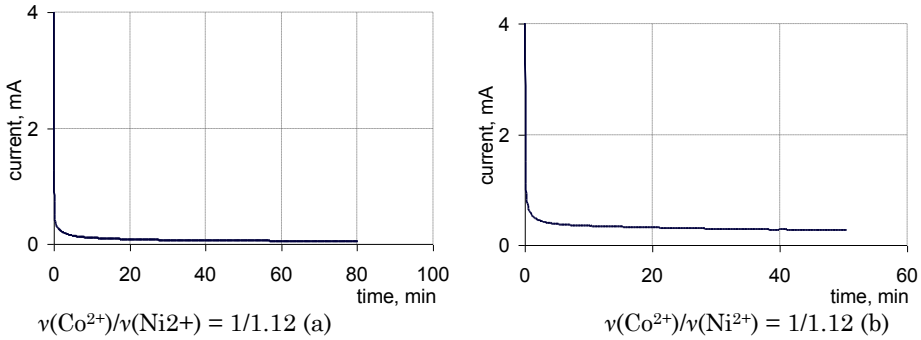


Fig. 4 – Chronoamperogramm of the electrochemical deposition of Co/Ni in the channels of the track etched membranes with the electrolyte composition $\nu(Co^{2+})/\nu(Ni^{2+}) = 1/1.12$ (a) and $\nu(Co^{2+})/\nu(Ni^{2+}) = 1/1.12$ (b)

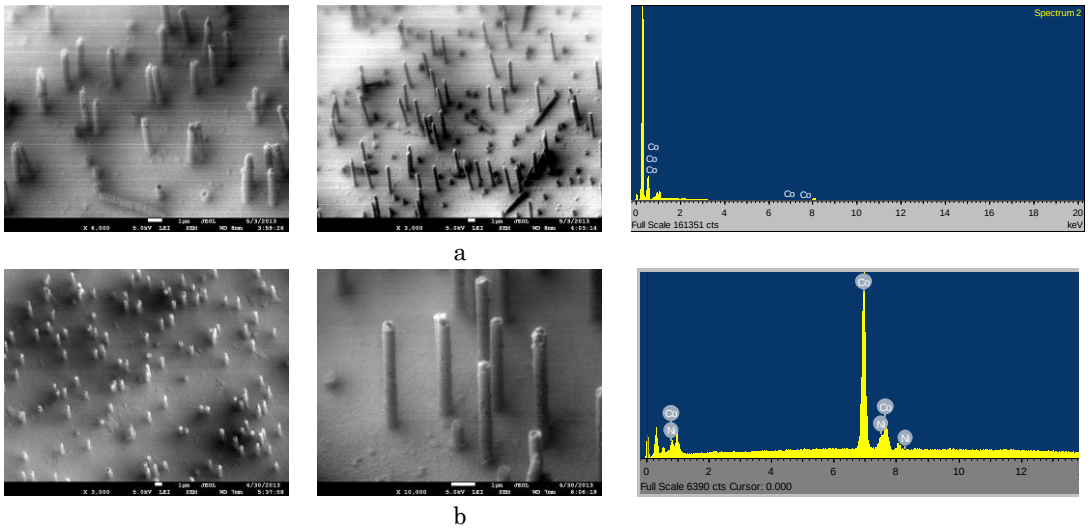


Fig. 5 – The SEM micrographs and EDA spectra of the synthesized nanotubes Co_{89}/Ni_{11} (a) and Co_{93}/Ni_7 (b)

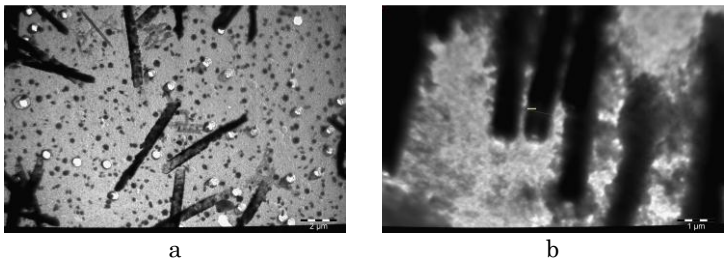


Fig. 6 – TEM micrographs of individual nanotubes Co_{89}/Ni_{11} (a) and Co_{93}/Ni_7 (b)

measured firstly, then subsequent deposition experiments terminated without reaching the temporary values, obtained in the "trial" experience.

Thus we have obtained Co/Ni nanotube arrays with diameter of 590 nm and a height from 4 up to 12 microns (Fig. 5). The EDA spectra shown in Fig. 5 revealed that the use of the electrolyte with the ratio $\nu(Co^{2+})/\nu(Ni^{2+}) = 1/1.12$ cause an atomic ratio of components in a nanotube 88.64/11.36 (%). In the case of $\nu(Co^{2+})/\nu(Ni^{2+}) = 1/1$ electrolyte, the ratio obtained for alloy is 93.38/6.62 (%).

Study of the structure of nanotubes by transmission electron microscopy (TEM) was also carried out. Some of the TEM images are shown in Fig. 6.

As seen from the TEM pictures (Fig.6), the all individual nanotubes Co_{89}/Ni_{11} (Fig. 6a) and Co_{93}/Ni_7 (Fig. 6b) have the same size along the entire length of the tubes. The thickness of nanotubes walls was approximately about 150-20 nm.

4. CONCLUSIONS

The template method has become a very simple yet prevailing process for the creation of nanomaterials. The etched PET membranes with pore diameters of 70 nm and 590 nm were used to fabricate Co/Ni micro-scale arrays by electrochemical deposition with various solutions. Obtained nanotubes have different composition that depends on composition of the electrolyte used for deposition.

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