Matrix Synthesis of Magnetic Nanowires

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In this work nanowires of magnetic metals (Co, Ni and Fe) were obtained via matrix synthesis, using etched track polymer template. The new data on electrodeposition of Ni was obtained. Two effects- the growth rate decrease (while the growing metal nanowires are filling the pores) and current density increase were investigated and discussed.

The results of X-rays analysis obtained using synchrotrone source demonstrated the dependence of structure and composition of nanowires on the deposition voltage. Mossbauer spectroscopy was used for investigation of Fe samples. The obtained data are in good agreement with X-rays results.

Keywords: Template synthesis, Electrodeposition, Nanowires, Synchrotron spectroscopy, Mossbauer spectroscopy.

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1. TEMPLATE SYNTHESIS

The matrix synthesis is known as one of the most perspective ways of production of nanomaterials. The main goal of this technique is to fill the pores with required substance. One of the best porous matrix version is track membrane. The track membrane application as porous matrix advantage is possibility to control the main geometric parameters of porous system at the stage of virgin film irradiation and at the stage of track chemical etching stage [1]. It is possible to fill the pores of track membrane with various materials. Among these materials, metals are most prospective. It must be noted that the electrodeposition (metal plating) is well-studied technological process, widely used in industry, but its peculiarities in the low volumes are investigated insufficiently.

Most promising metals are magnetic ones – the obtained ensembles of magnetic nanowires could be used as sensors, as the media for magnetic memory. Moreover, these samples are of great scientific interest due to the possibility to vary the geometry of the samples on nanometer scale. In this work the Co, Ni and Fe electrodeposition into track membranes pores with diameters in range from 0.1 mcm to 0.5 mcm was carried out. (It could be mentioned that our first results for application of such nanowires as ion emitters were given in [2,3], for obtaining of Co and Ni nanowires are given in [4,5,6]). Here the metals deposition was done in potentiostatic regimes and the dependence of current on time was measured. The obtained results for Ni are given in Fig.1 – they are in a good accordance with the data for Co [4].

Two effects are of great interest here: the growth rate decrease (while the growing metal nanowires are filling the pores) and current density increase (to compare with a flat surface).

In order to explain the first effect we should note that two processes competition takes place in the growth of metal replicas in narrow pores – the decrease of unfilled pore section length and the decrease of electrolyte concentration in narrow channels (because of slow ion transport, so called diffusion limits). The first effect results in electrical resistance decrease while the second one – to its increase. It is clearly that growth slowdown proves the second process dominance. This conclusion is suggested with the fact that this effect is maximal for narrow pores and/or under high overvoltage.

The increase of current density was observed in metal replicas growth in matrix pores. It must be noted that increase of effective electrolyte conductivity in the track membranes pores was observed earlier. This fact was explained with gel layer formation at the pore surface [7, 8]. It may be suggested that current density increase defined in work presented can be explained with gel layer existing at pore surface. The one’s high conductivity results in increase of measured conductivity by several times with compare to standard one.

The production of Fe nanowires was also investigated. The influences of solution mixing, overvoltage and temperature on the process were studied.
2. STRUCTURE INVESTIGATIONS

Structure investigations were done for Fe, Co and Ni samples using synchrotron source (“Belok” station of the Synchrotron in Kurchatov institute, wavelength 0,09811 nm). Measurement technique described in [9]. The obtained results are given in Fig. 2 and 3.

In all cases two types of peaks could be indicated: a substrate (copper) lines and the lines of the metal deposited into the pores. For iron samples, increasing of deposition voltage leads to decreasing of iron lines intensity; for the highest voltage (1050 mV) iron was not detected. For nickel samples the trend is the same (see spectra 2 and 3 in Fig E), but the effect is not so significant. For cobalt samples two type of phases were detected – cubic and hexagonal.

3. MOSSBAUER SPECTROSCOPY

Iron samples were investigated by Mossbauer spectroscopy. This technique was used for templatesynthesized Fe nanowires before (see for example [6] and previous papers of these authors), but all of these experiments were carried out for the wires grown in the POA (porous oxide aluminum) matrices. In our experiments matrix and growth parameters were quite different. We investigated Fe nanowires grown inside the 100 nm pores (etched tracks in PET film) under three different overpotentials (overvoltages) from -600 to -900 mV.

The Mössbauer absorption spectra from 57Fe nuclei were recorded at the temperature 295 K using a stand-
ard MS-1104Em spectrometer (University Rostov-on-Don, Russia), operating in the constant acceleration mode. The vibrating source of γ-quanta [57Co(Rd)] was at room temperature. Isomer shifts were measured relative to the reference α-Fe sample (18-μm-thick iron foil annealed in hydrogen) at room temperature. Computer processing of spectra was carried out using University MS software. The room temperature Mössbauer spectra for three samples are shown in Fig. 4 – for -600 mV, in Fig.5 – for -750 mV and in Fig. 6 – for -900 mV.

In the first case we have sextet-spectra consists of 6 peaks with intensity ratio 3:2:1:1:1:3. This ratio is typical for the polycrystalline or powder pure α-Fe sample with disoriented domains magnetization without any texture. At the same time, increasing of overvoltage (next sample, Fig 5) leads to changing of the peaks intensity – now it is approximately 3:1:1:1:1:3. The computer data processing revealed in this case the presence of one magnetic sextet corresponding magnetic ordered α-Fe phase. It could be connected with orientation of iron domain magnetization (approx. 37° to direction of γ-quanta). And in the third case (Fig. 6 – the highest overvoltage) additional paramagnetic doublet indicates the appearance of some additional phases (probably oxides FeO and α-Fe₂O₃ or sulphides).

These Mossbauer spectra and structure data for Fe and are in good agreement: the process at low voltage gave the perfect crystalline wires (no impurities, no magnetization). At the same time, the increasing of overvoltage (and therefore the acceleration of nanowires growth) leads to formation of the wires with anisotropy and/or with impurities.

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