Two types of 3-d metals nanowires: synthesis, structure and properties

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Abstract. Matrix synthesis based on etched-track membranes was used for fabrication of two type of nanowires (NWs) – homogeneous (alloys – Fe-Co and Fe-Ni) and heterogeneous – layered NWs (Ni/Cu and Co/Cu). Parameters of galvanic process and features of electrodeposition were determined. X-ray analysis demonstrated the two-phase structure of alloys with low concentration of Fe and step-type changing of cell-parameter with changing of metals concentration ratio in alloy NWs. Topography of NWs was determined by SEM: NWs’ diameter were higher than pores size due to metal oxidation or expansion. Elemental analysis demonstrated that composition of Fe-Co NWs is equal to composition of electrolyte, while for Fe-Ni Fe concentration in NWs is higher; this difference increases with concentration of Fe. TEM allows to evaluate the length of metal segments in layer NWs, to estimate their concentration (pure Cu and mixed Co or Ni). Magnetic-Force microscopy allows to correspond structure and domain size. External field could change magnetization, but only partly – due to mutual influence of NWs.

1. Introduction
Development and application of nanomaterials is one of the main trends now. Among them nanowires (1D-structures) are of great interest due to interesting properties and possible applications. Such structures could be obtained by matrix synthesis technique: pores in special matrix are filled by desired material. Some porous media – track etched membranes, porous alumina, zeolites, porous silica – could be used as template. Two main types of deposition process are known and used – chemical and electrochemical.

This approach was first used by Possin [1], who deposited metals into the pores of mica. Then polymer track etched matrixes were used as templates [2]. Then different types of two-and many-components samples were synthesized [3,4,5,6]. In 1995 porous alumina (PA) with nanosize cylindrical pores was obtained [7]. So, since that time many works were devoted to fabrication of nanowires based on PA. Nevertheless, track membranes are still in use in template-processes.

It should be noted that electroplating technique in both type of matrixes gave possibility to obtain different types of nanostructures due to possibility to change the process parameters in wide range. This
work is devoted to fabrication of NWs from 3-d metals (Cu and iron-group metals-Fe, Co and Ni) using track membrane as template and electrodeposition as a method of “filling” the pores.

Magnetic NWs were obtained by matrix synthesis technique, using etched track membranes as templates. Two types of NWs were obtained – homogeneous alloys (Fe-Co and Fe-Ni) and layered NWs (Ni/Cu and Co/Cu) were electrodeposited into the pores of PET membrane.

2.  Experiment

2.1.  Matrix

Etched track membranes: PET films with thickness 10 μm, pores diameter 100 nm and density 10⁹ per sq.sm (JINR, Dubna), were used as templates.

2.2.  Electrodeposition of alloy NWs

To obtain FeNi alloys, an electrolyte of the following composition was used: NiSO₄ • 7H₂O - 16 g/l, NiCl₂ • 6H₂O - 40 g/l, H₃BO₃ - 25 g/l, C₆H₈O₆ - 1 g/l, sodium lauryl sulphate - 1 g/l. The variation of composition of NWs was achieved by varying the concentration of FeSO₄ • 7H₂O in the electrolyte from 4 to 32 g/l. The deposition potential in all cases was 1.5 V. An iron anode was used. For alloy FeCo NWs the composition of electrolyte was used: CoSO₄ • 7H₂O - 16 g/l, CoCl₂ • 6H₂O - 40 g/l, H₃BO₃ - 25 g/l, C₆H₈O₆ - 1 g/l. The composition of NWs was varied by changing of the concentration of FeSO₄ • 7H₂O in the electrolyte from 4 to 72 g/l. During the deposition of alloy NWs the dependences of the current on time were plotted. These dependences were approximately the same for both types of NWs (FeNi and FeCo).

2.3.  Electrodeposition of layer NWs

For obtaining of heterostructured NWs it was necessary to use an electrolyte containing at least two types of metal ions. In this work the mixtures of two electrolytes were used. In both cases, the material with the lowest deposition potential was copper. The second metals were nickel or cobalt. For synthesis of Cu/Ni layered NWs the electrolyte was: NiSO₄ • 7H₂O – 196.7 g/l, CuSO₄ • 5H₂O – 6.25 g/l, H₃BO₃ – 31.6 g/l. For synthesis of Co/Ni layered NWs: CoSO₄ • 7H₂O – 200 g/l, CuSO₄ • 5H₂O – 8 g/l, H₃BO₃ – 40 g/l. The alteration of concentration in different layers could be obtained by changing of deposition potential. Firstly, the deposition was carried out on a flat surface at different potentials in order to estimate the optimal potentials. For this, electrodeposition was carried out on a flat surface. The potential varied stepwise from sample to sample.

2.4.  Structure

The structure of obtained NWs was investigated by X-ray analysis (diffractometer Rigacu Miniflex600). For homogeneous NWs (FeNi alloy) with a low concentration of Fe two different phases were detected: solid solutions FeNi and pure Ni. The pure Ni phase was not detected in the samples with higher concentration of Fe. X-ray data of the samples are shown in the figure 1.

The lattice parameter of the alloy FeNi shifted toward iron with increasing iron concentration. Changes were insignificant (on the verge of instrument error).

The study also investigated the crystal lattice of the samples obtained during the development of the regimes for producing heterostructure nanowires. The results are presented in figure 2.

Samples of heterostructural nanowires were studied by X-ray analysis. In this case, the results were compared with thin layered films obtained by the electrodeposition method. The results indicate a decrease in the linear size of crystallites in nanowires.

2.5.  Scanning Microscopy

SEM analysis shown that all NWs have diameter higher than pores one (NWs with diameter 110-120 nm were grown in 100 nm pores). One reason is the formation of an oxide film during contact with air, another – expansion of metal inside the narrow pores channels. The length of alloys NWs corresponds
to the thickness of the matrix (10 microns). Examples of microphotographs of arrays of FeCo alloys nanowires are shown in the figure 3.

Figure 1. X-ray data of nanowires of alloy FeNi: a) 4 g/l of FeSO₄•7H₂O; b) 32 g/l of FeSO₄•7H₂O.

Figure 2. Lattice constant obtained from X-ray data of the samples obtained during the development of the regimes for producing heterostructure nanowires.

2.6. Elemental analysis
The composition of metal ions in different grown electrolytes were calculated. At the same time, the composition of corresponding NWs was estimated by X-rays elemental analysis. The obtained results - dependences of these compositions for both metals on concentration of Fe in electrolyte (for FeNi and FeCo NWs) - are given in figure 4.

One can see significant differences in the dependences of the elemental composition of the NWs on the electrolyte composition for FeNi and FeCo. For the case of FeCo NWs, these differences were not noticeable. The concentration of iron in the NWs slowly increases with increasing concentration of Fe salt in the electrolyte. In this case, the difference between the concentrations of iron in NWs and the iron content in the electrolyte gradually increases: from zero (at minimal concentration) to 11% (for the maximal level of FeSO₄). For the case of the deposition of FeNi NWs, the difference between the concentrations of iron atoms in NWs and the iron ions of the electrolyte increases significant with increasing concentration of Fe salt in the electrolyte. (The initial difference (at the lowest concentration of FeSO₄•7H₂O) is 10%, while the maximum difference is 35%). It could be explained by the effect of abnormal iron co-deposition of Fe.
Figure 3. Microphotographs of arrays of FeCo alloys nanowires.

Figure 4. Elemental analysis of nanowires and ion concentrations in the electrolyte: a) FeNi b) FeCo.

Samples obtained by deposition on a flat surface during the deposition of Cu/Ni, Cu/Co electrolytes were examined using SEM. The results of the elemental analysis are presented in figure 5.

The changes in the elemental analysis coincide with the lattice the parameters. So, the potential for deposition of a copper layer was found to be equal to 0.8 V (in all cases), while optimal potentials for deposition of a nickel or cobalt layer were 1.8 V. Using the data obtained, the deposition was carried out in the pores of the matrix. It was shown in the work [8]. That when the potential is switched depending on time (the time of deposition of one layer is the same), the thickness of the layers changes along the length of the nanowire. After receiving the samples were investigated by the method of SEM. The results are presented in figure 6.

Element mapping determined the concentration for example, in Ni/Cu NWs there were layers of pure Cu and Ni-based alloy (83% Ni and 17% Cu). TEM with diffraction analysis demonstrated the polycrystalline structure of NWs with fraction of small crystals (5-10 nm) and bigger crystals (50-80 nm). Ni (Fm3m), Cu (Fm3m) and oxides (Cu2O and CuO) were determined.
Figure 5. Elemental analysis of samples obtained by deposition on a flat surface during the deposition of Cu/Ni.

One can see the separate layers. For a more accurate analysis of the study was conducted by the method of TEM. TEM images of obtained NWs are given in figure 7.

Figure 6. SEM of Cu/Ni nanowires.

Figure 7. TEM pictures of layer NWs: Ni/Cu (a) and Co/Cu (b).
3. Magnetic measurements

3.1. Magnetometry

Magnetometry of alloy NWs were carried out in our previous work [9, 10]: Hysteresis loops were measured, and it was shown that all samples were ferromagnetic. According to hysteresis curves Fe-Co NWs are hard magnetics: coercivity is 1100 Oe, while Fe-Ni NWs (with 100 nm diameter) have “soft” magnetic – coercivity less than 100 Oe. Dependence on diameter was also demonstrated-Ni-Fe NWs with small diameter (30 nm) demonstrated hard magnetic parameters. The difference between hysteresis loops measured “in-plane” and “out-of-plane” geometries was also found.

3.2. Scanning Probe Microscopy

The distribution of the magnetization in the single NW was studied using a Solver P47Pro (NT-MDT) scanning probe microscope (SPM). The mode of SPM – magnetic force microscopy (MFM) measurement – was carried out using standard commercial NSC 18/Co-Cr (Micro-Science) cantilevers. The one-pass technique was used. MFM probe is positioned at the distance of several dozen nanometers far from the sample surface. It was done in order to avoid the magnetization by magnetic field of the probe. Electromagnet was placed near the sample- so, MFM measurements was carried out in external magnetic field. Two types of measurements were done.

The “vertical” NWs embedded in polymer matrix were tested in [11]. It was found that magnetization of adjacent NWs is different, the magnetization (in general) could be change by external field (up to 0.2 T). But even for the highest field the identical magnetization (with the same orientation of all NWs) couldn’t be obtained. It could be explained by mutual demagnetization of neighbouring NWs.

Here the horizontally fixed layer NWs were investigated using the same unit. In this case the problem of “fixation” of horizontal NWs at the surface was solved. Three types of “adhesion” were tested. The first one was simply deposition of NWs powder at the surface – NWs were attached to the surface, but part of them were removed during scanning in SPM. The next one was fixation of NWs at the glue dispersed at the surface of the sample holder. Three types of glues were tested, but in all cases NWs position wasn’t horizontal and part of them were full covered by the glue. Only third approach gave positive result: NWs deposited at the holder-surface were covered by thin Cu layer by thermal-deposition (this is process, usually used for metallization of membranes surface for creation of conductive layer).

The “horizontal” single Ni/Cu NWs fixed on the substrate surface were examined using SPM operating in atomic force microscopy (AFM) mode and in the magnetic force microscopy mode (MFM). For such NWs the domain structure and layer structure were detected – see figure 8, for NWs with segment length 100 nm and 250 nm. Using AFM, it was found that the NWs obtained have “broadenings” that could be associated with alternating layers of Ni and Cu (figure 8a). The pair, consisting of a layer of Ni and Cu, formed one segment of NW.

MFM measurements in the absence of an external magnetic field showed that NWs have a “band-like” magnetic distribution — an alternation of light and dark areas of approximately the same length on the MFM image (figure 8b). The length of such sections is longer than the length of the magnetic layer and longer than the segment length. The direction of magnetization in adjacent areas covering several segments does not always coincide with each other. This leads to the appearance on the MFM image of different lengths of neighbouring areas.

For these samples external field was also applied and was varied in the range from -165 Oe to +165 Oe. The application of an external magnetic field of ± 165 Oe along the axis of such NWs leads to a redistribution of the magnetization in it. Despite on the fact that the fields were directed along the easy axis of magnetization of NWs, it cannot be completely remagnetized by such fields.

So, it can be concluded that NWs have topographic features due to the alternation of layers of magnetic and nonmagnetic materials. Such NWs have a complex magnetic distribution in the form of alternating bands - a strip structure. The length of such bands is longer than the length of a separate
magnetic layer and can include several segments. The application of an external magnetic field of ±165 Oe along the axis of easy magnetization NW leads only to a redistribution of magnetization in it.

Figure 8. Probe Microscopy of single Ni/Cu NW: a,b – NWs with 100 nm segments; c, d – NWs with 250 nm segments: AFM-topography (a, c), MFM (b, d).

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