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Specific Features of Obtaining of Metal Nanowires by Replication of Pores of Track Etched Membranes

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Abstract. Ensembles (massives) of metal nanowires (with diameters 50-200 nm) were obtained using method of template synthesis. Polymer track etched matrixes were used as template. Nanowires obtained were the replicas of the pores in these membranes. The problems of choosing of electrolyte and different regimes of electrodeposition were discussed. Different techniques of separation of obtained nanowires from growth polymer matrix were used- etching at elevated temperature, ultrasound and UV-treatment. The regimes of obtaining of layer Cu/Ni nanowires were investigated and the optimal voltages were found: 0.8 V for Cu-layer and 1.8 for Ni layer. It was also found that application of magnetic field accelerate the process of electrodeposition; moreover, application of SOUTH pole leads to formation of hollow Ni-layers. Using of "two-bath" method of electrodeposition found to be optimal for obtaining of two-parts wires. Such wires could be used for generation of THz irradiation.

Introduction

One of the promising applications of radiation technologies is the production of special matrices for template synthesis, for obtaining arrays of a special type of nanoobjects-nanowires. In this paper, we consider some features of the use of track matrices in this process.

In general, the production of nanomaterials is one of the key areas of science and technology. Among the many different types of nanomaterials, one-dimensional nanowires (nanorods) are of particular interest. One of the promising methods of obtaining such objects is the method of matrix (template) synthesis. The basic idea of the approach consists in a two-stage synthesis. At the first stage a special porous matrix with a big number of identical nano-sized pores is made. The pores in such a matrix are then filled with the required material, which forms the replicas of the pore channels. This method allows to obtain the arrays (ensembles) from a large number (up to 10^{10} per cm^2) of nanowires (NWs), identical in geometry - diameter and length. Note that various materials, porous silicates, porous alumina, polymeric track membranes can be used as a matrix. Materials "loaded" in the pores, can also be very different - semiconductors, polymers, water-soluble crystals, metals. The type of material determines the "loading" method, which can be very different, from mechanical to chemical and electrochemical.

The idea of obtaining the pores replicas was first realized in [1], where the author galvanicaly deposited the tin into the pores of mica. The paper [2] describes how cobalt and nickel were successfully deposited in a porous oxide matrix; there it was suggested to use such structures in magnetic recording devices. In subsequent works, the electrodeposition of the metals was carried out already in the track pores of polymer matrices [3–5]. The basic ideas of the method of matrix synthesis are described in detail in the famous review by Martin [6]. In subsequent years, many researchers worked out methods for obtaining replicas of pore channels and the synthesis of NWs from various metals.

In the present work, polymeric track membranes were used as the matrix, in the pores of which NWs from metals – primarily metals of the iron group (cobalt, nickel and iron) were deposited by electrochemical (galvanic) method.

It should be noted that electrochemical deposition is one of the oldest and proven technological processes. Its undoubted advantage is the ability to regulate the main parameters of the process within a wide range and the high repeatability of the results in a classical process. This process was successfully implemented when the metal was filled into the pores of track membranes at the end of the last century [7, 8]. Despite the fact that a large number of works were subsequently published, practically no attention was paid to the methodological aspects of obtaining nanowires. In many cases, the details of the process were simply not described by the authors. Because of this, there are many difficulties in comparing of the results obtained by different authors and poor reproducibility of the results.

In this paper, we consider a number of methodological features of several main stages of obtaining NP arrays: the stage of obtaining the matrix, the stage of choosing the electrolyte, the actual galvanic process, and finally, the separation of the synthesized massive of NWs from the growth polymer matrix.

Experimental

The Matrix. Polymer track membranes are traditionally used as matrices. The latter are obtained by irradiation of the polymer film with accelerated heavy ions (at this stage, the so-called latent tracks are formed) and subsequent etching in an alkaline solution (while latent tracks are converted into through pores). The production of track membranes is a semi-industrial process now. It should be noted here that usually track membranes are made for the needs of fine filtration, for which the pore density should be maximal, and the pores themselves are not parallel (they usually have a wide spread in directions to reduce the probability of crossing). Matrix synthesis, as a rule, requires membrane-matrices with parallel pore channels and (as a rule) with a relatively low pore density. Thus, industrial track membranes are not always optimal and for the synthesis of nanowires it is necessary to manufacture special matrices. Such matrices are made of a polymer film irradiated in a special way: irradiation is carried out strictly perpendicular to the surface and with a relatively small dose of 106 -107 ions per square cm. In some cases, the subsequent obtaining of the through-pores is not required, and the "dead-end" pores are used. Thus, the materials obtained are no longer strictly speaking membranes - it is more correct to call them track matrices.

The material of track membranes in Russia is traditionally polyethylene terephthalate (PET), while polycarbonate (PC) is more often used in the West. These polymers are similar in structure and type of chemical treatment, but there are some differences. So, after etching of the irradiated PC formed pores have smoother walls than in PET. We note that for filtration process the first option is more desirable, while in order to obtain magnetic structures the "nonsmooth" walls are preferred.

Electrolytes. Electrolyte selection is the key point of matrix synthesis. A lot of articles and reviews are devoted to this question, of which it can be noted - [9].

Here only a few points could be mentioned. The basis of the electrolyte is the salt (of the metal that needs to be precipitated). Most often, sulfate salts are used, one of the advantages of which is their good solubility. In the case of a multicomponent composition mixture of salts is used. In addition to salts, acids can be added to the electrolyte (for increasing the electrical conductivity of the solution), buffer additives (to maintain the necessary acidity). Ascorbic acid and lauryl sulfate are also used. The composition of electrolytes can vary greatly depending on the solution The choice of the electrolyte and the choice of the deposition regime may depend on the choice of the anode. It is possible to use an insoluble anode (for example, coal anode) - however, there arises the problem of changing the composition of the electrolyte-enhancing it by the ions of the metal being deposited. Most often the anode used is made of the same metal that is deposited during the synthesis, while dissolving the anode compensates for the loss of metal ions due to electrodeposition. However, in this case, there is a risk contamination of the solution with impurities frequently present in the anode, and the problem of compensation for outgoing ions is not solved in this case when depositing a multicomponent (two-component) material.

The process of electrodeposition is carried out in a special galvanic cell. Often, the electrolyte is stirred to accelerate the diffusion process in the cell and to remove gas bubbles formed at the "mouths" of the pores and blocking the ion transport. The process itself can be carried out in different modes - usually galvanostatic (at constant current) and potentiostatic (at a constant potential). The latter mode is used more often: during the process in this case, the current versus time is recorded - the potentiostatic curve. The latter allows monitoring of the process and displays various stages of electrodeposition. Thus, the onset of a sharp increase in current usually means that the pore channel is completely filled and the growth of the metal outside the matrix begins, usually the process should be stopped at this time or earlier.

Separation of the Growth Matrix. The resultant polymer matrix with inserted metal filaments-nanowires is a kind of metal-polymer composite. This composite can be investigated and used in a number of applications. However, in most cases, the polymer matrix must be removed, releasing the formed "array" (ensemble) of free-standing NWs. Typically, the polymer is removed by dissolving in concentrated alkali at the high temperature. Often, after removal of the polymer matrix, polymer fragments still remain between thin NWs, especially in the case of NWs with small diameters and high surface densities. In this case, sometimes ultrasound treatment is used- during etching or after it. But after these processes of “hard” removing of matrix, the resulting wires can be damaged. To "soften" the process, there is a preliminary "embrittlement" of the polymer: it is treated with UV irradiation (λ = 320 nm, 24 hours), after which the polymer is removed much more easily. We also developed the method of pre-etching of the matrix, after which it can be removed mechanically.

Obtaining of Layer Cu/Ni Nanowires. It is known that it is possible to obtain heterogeneous layer NWs (structures from alternating layers of different metals) by changing the deposition potential. Thus, during electrodeposition from an electrolyte containing ions of two metals initially (at a low voltage), a metal with a lower equilibrium deposition potential will precipitate, then (with increasing voltage) a metal with a higher equilibrium potential will be deposited. In the latter case, an "alloy" of two metals will form; the ratio of the components in such alloy can be varied by changing the concentration ratio in the electrolyte.

In this paper, the deposition regimes of Cu / Ni layer structures were determined. For this purpose an electrolyte of the following composition was used: $NiSO_4 \cdot 7H_2O$ - 200 g / l; $CuSO_4 \cdot 5H_2O$ – 6 g / l; H_3BO_3 – 30 g / l. First, the deposition was carried out on a flat surface. A series of samples was obtained, with the potential varying stepwise from 0.2 V to 3 V (with 0.2 V steps). After preparation, the samples were examined on a scanning electron microscope with elemental analysis. Figure 1 shows the dependences of the atomic concentration of nickel and copper for samples with different deposition potentials.

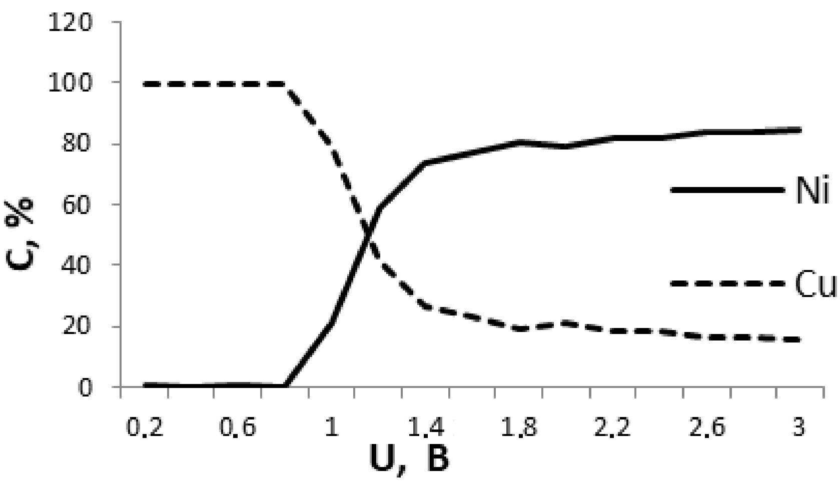

Figure 1. Graphs of the dependence of the composition of the sample on the growth voltage.

It can be seen that at a potential up to 0.8 V the nickel concentration is zero, then starting from 1 V it rises sharply and at a potential of 1.8 V goes to the "plateau" (nickel concentration: 80÷83%). At the same time, the concentration of copper after 0.8 V sharply decreases. Thus, it can be concluded that the optimal potential for copper deposition is 0.8 V, and for deposition of nickel-1.8 V. According to microscopic data, deposition at these potentials gives a good surface quality. Note that with the growth of the potential the ratio of the elements does not change, only a slight acceleration of the process took place, but the surface becomes much more loose -t.e. increasing the potential is undesirable. The obtained parameters were then successfully used for the growth of NWs arrays of Cu/Ni layer structures.

Influence of Magnetic Field. Of great interest are the problems of direct influence on the growth of nanowires during the electrodeposition. As one of the possibilities it is application of the magnetic field. The effect of the magnetic field during the growth of the NWs array was studied for the above-mentioned ensembles of the Cu / Ni layer structures, as well as for the NiFe (Ni-50%, Fe-50%) alloy. During electrodeposition, a permanent magnet was attached to the growth matrix from the back side. We used a neodymium magnet with a magnetic induction of 0.25 T, which was applied sequentially both by the south and north pole. The deposition curves obtained for both types of samples, for two directions of the magnetic field, and for control samples grown without application of the field, are presented in Figure 2.

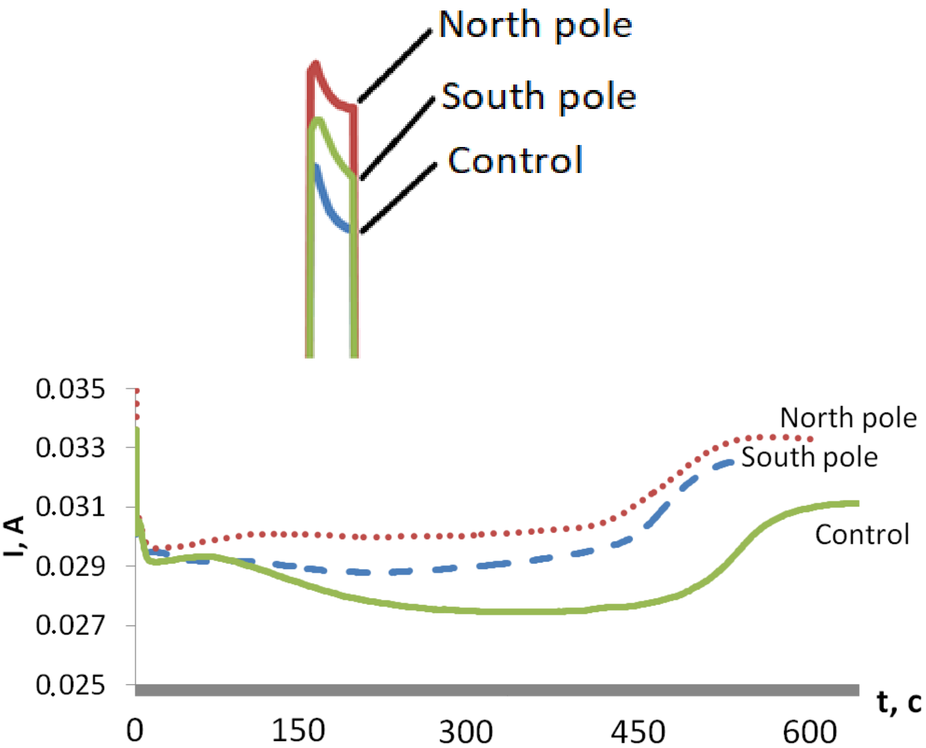

Figure 2. Graph of current versus time for growth for various orientations of the external magnetic field: a - growth of layer structures (fragment of the graph is the "top" of one peak for different orientation of external field and without field-Control), b - growth of alloys.

It can be seen that the magnetic field has a significant effect on the deposition process: the application of the field accelerates the process, and with the application of the northern pole the growth rate is higher (for both cases- deposition of alloy and layered structure). Preliminary X-ray examinations of the obtained NWs alloy were carried out. It is shown that the application of a magnetic field during the growth of an alloy leads to a change in the ratio of the X-ray lines intensity. So, the appearance of the texture could be supposed. The resulting arrays were then separated from the growth matrix and studied with the electron microscope. These studies have shown that the magnetic field has practically no effect on the shape of the alloy NWs. At the same time, a strong influence on the topography of layer NPs was found. Thus, at the tops of the NWs grown at the application of the south pole, hollows (cavities) were found, and the NWs in this part has the shape of a “tube”. This part of the NWs corresponds to the nickel layer, which grew at a greater potential. Proceeding from this, it can be assumed that all layers of nickel are also hollow inside and "sealed" by the layers of copper then deposited, thus forming a kind of capsule. In the sample of NWs, to which a south pole magnet was applied during growth, no formation of cavities was observed. However, the length of the NWs in this case increases noticeably comparison with a sample grown without applying a magnetic field. This is due to the increase of curren during the growth of the array.

“Two – Bath” Deposition. The samples of NWs, consisting of only two layers, were also obtained in this work. For this case, two methods of forming layer structures were compared: "Single-bath" and "double-bath". In the first of these, described above, the process was carried out "in one bath" - in one electrolyte containing ions of two metals. In the second case, the growth of wo metals is carried out sequentially in two different electrolytes with different ions ("in two baths"). The second method is now practically not used for the preparation of layer NWs because of possible problems associated with the change of electrolyte and the resulting plugging of individual pores. However, a comparison of the results obtained in the work showed that the "two-bar" method produced better results, in particular, because of the possibility of obtaining "clean layers" (without the admixture of the second metal). Moreover, this approach gave possibility of sequential separate deposition of metals with close deposition potentials- such as Ni and Co. Thus, this method (which historically was the first in the production of multilayer coatings on a flat surface) showed its advantage, at least with the growth of NPs consisting of two layers (two parts) and, accordingly, requiring only one change of electrolyte. Note that structures consisting of two layers, for example, including contact of metals with different magnetic properties, now attract a lot of attention. Thus, in our work [10], the possibility of generating terahertz radiation was shown when a high-density current was flow through such a structure.

Summary

The paper shows the possibilities of the matrix synthesis method for obtaining of nanowires of different types, including layer structures. External magnetic field was shown to be effective to vary the NWs parameters.

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References

[1] G.E. Possin, A method of forming of very small diameter wires, Rev. Sci. Instrum. 41(5) (1970) 772–774.

[2] S. Kawai, R.J. Ueda, Magnetic Properties of Anodic Oxide Coatings on Aluminum Containing Electrodeposited Co and Co-Ni, J. Electrochem. Soc. 112 (1975) 32–36.

[3] S.K. Chakarvarti, J. Vetter, Morphology of etched pores and microstructures fabricated from nuclear track filters, Nucl. Instr. Meth. Phys. Res. 62(1) (1991) 109–115.

[4] J. Vetter, R. Spohr, Application of ion track membranes for preparation of metallic microstructures, Nucl. Instr. Meth. Phys. Res.79(1-4) (1993) 691–694.

[5] T.M. Whitney, J.S. Jiang, P.C. Searson, C.L. Chien, Fabrication and Magnetic Properties of Arrays of Metallic Nanowires Science 261(5126) (1993) 1316–1319.

[6] C.R. Martin, Nanomaterials: A membrane based synthetic approach, Science 266(5193) (1994) 1961–1966.

[7] N. Lupu (ed.), Electrodeposited nanowires and Their Applications, InTech, Croatia, 2010.

[8] M. Va´zquez (ed.), Magnetic Nano- and Microwires: Design, Synthesis, Properties and Applications, Woodhead Publishing, Elsevier, 2015.

[9] A.A. Davydov, V.M. Volgin, Template Electrodeposition of Metals, Electrochemistry 52(9) (2016) 905-933 (in Russian).

[10] S.G. Chigarev, E.A. Vilkov, G.M. Mikhailov, A.V. Chernykh, D.L. Zagorsky, S.A. Bedin, I.M. Doludenko, A.S. Shatalov, Spin-inject Generators of THz-irradiation based on nanostructures, In: Proc. of V All-Russian Microwave Conference, Moscow, Russia (2017) 195-197 (in Russian).