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on Advanced Materials and Technologies

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内 容 提 要

本书收录了第十四届中俄双边新材料新工艺研讨会提交的全部论文，内容涵盖了纳米材料、稀有金属和合金、新能源和储能材料、电子信息材料、生物医用材料、航空航天材料、表面工程技术、陶瓷复合材料、新型冶金工艺和材料加工技术等领域。

本书可供材料及其加工领域的科研、技术和管理人员阅读，也可供大专院校有关师生参考。

Brief Introduction

The book contains all the papers submitted to the 14th Sino-Russia symposium on advanced materials and technologies. The topic to be discussed covers from nanomaterials, rare metals and alloys, new energy and energy-saving materials, electronic information materials, biological and polymer materials, aerospace materials and surface engineering technology, ceramic and composite materials, new metallurgical processes to materials processing technology.

This book can be used for researchers, technicists and managers in materials and processing fields and teachers and students in universities.

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The Problems of Obtaining Multilayer Nanowires Ni/Cu

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ABSTRACT: The present work is devoted to obtaining multilayer nanowires by electrochemical filling of polymer matrices obtained by track technology. In this work, the optimal regimes of electrodeposition of nickel and copper were determined experimentally-based on the deposition of continuous layers from two-component solutions. On the basis of these data, thin layers of variable composition were obtained, and then-heterostructured nanowires (NW) consisting of alternating layers of Ni / Cu multilayers. Investigation of the structure and composition of the deposited layers and NW was carried out using the method of scanning electron microscopy and point element analysis.

1 Introduction

In recent years, nanostructured materials, including composition-modulated alloys, have been widely studied. These materials, with the thickness of individual layers less than 100 nm, have very interesting properties, unattainable in bulk materials. The method of matrix synthesis, using track membranes as a matrix, makes it possible to obtain such structures in the form of thin rods (nanowires) consisting of the above alternating layers.

The possibilities of using such structures seem very promising. Thus, magnetoelectric properties are of great interest [1, 2]. A number of works also consider the possibility of using special tribological and mechanical properties of such surfaces [3-6]. We note that many metal multilayer materials were obtained using vacuum technologies [7,8], but, in our opinion, the application of these methods is limited by their high cost.

Recent studies have shown that electrodeposition is a very valuable method for obtaining metallic multilayers [9-11]. Despite some limitations (for example, the need to use aqueous solutions, the inability for some metals to precipitate from electrolytes), the electrochemical method has been successfully used to produce multilayer systems such as Ni / Cu, NiCo / Cu [12] Co / Cu [13], NiFe/Cu [14], Co / Pt [15].

The purpose of this work was to refine the regime for obtaining an array of heterostructured nanowires of Cu / Ni composition and to study them using a scanning electron microscope with an attachment for elemental analysis. The main problems that have been solved in this paper are the selection of a two-component electrolyte, the determination of the optimum deposition potentials of each metal, the selection of modes for the growth of nanowires, and the confirmation of the presence of layers.

2 Metal deposition on a flat surface

Table 1

Element	Concentration
$NiSO_4 \cdot 7H_2O$	196.7 g/L
$CuSO_4 \cdot 5H_2O$	6.25 g/L
H_3BO_3	31.6 g/L

The composition of the electrolyte (Table 1) used in the work was selected on the basis that Ni has a higher equilibrium deposition potential, therefore, Cu will be precipitated in pure form at a lower potential applied to the plating bath. If the potential is increased, a simultaneous separation of the two metals takes place

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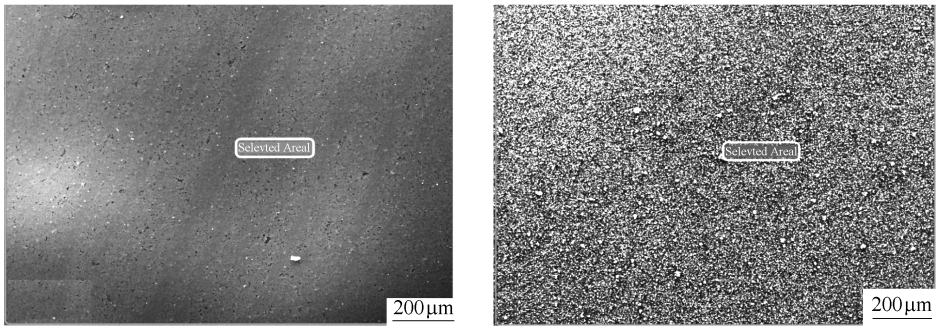
and a predominant deposition of nickel can be achieved by significantly increasing its concentration in the solution.

For deposition, a standard galvanic cell was used, as a power source was taken programmable potentiostat-galvanostat Elins P-30S. Copper plate was used as an anode.

To determine the optimum deposition potentials of Ni and Cu, it was necessary to determine the composition of the precipitated substance at different potentials. At this stage, the electrodeposition was carried out on a flat surface at potentials from 0.2 to 3 V in steps of 0.2 V. The deposition time was 10 minutes. Metal deposition took place at room temperature. After the preparation, the samples were examined on an FEI Quanta 650 electron microscope with an EDAX prefix for elemental analysis (IPM RAS). The resulting surface images are shown in Fig. 1.



0.4V 1.8V

Fig.1 Images of the surface of samples obtained at different deposition potentials

A study of the microstructure of the samples showed that with increasing stress, the surface of the metal becomes more loose. This is due to an increase in the rate of growth of the deposited material. The results of elemental analysis of samples, in addition to nickel and copper, showed the presence of oxygen and gold. The presence of oxygen is associated with oxidation of the sample in air, the presence of gold is explained by the fact that the substrate material consists of it. We note that as the growth potential increases, the atomic concentrations of oxygen and gold in the semiconductor layer decrease.

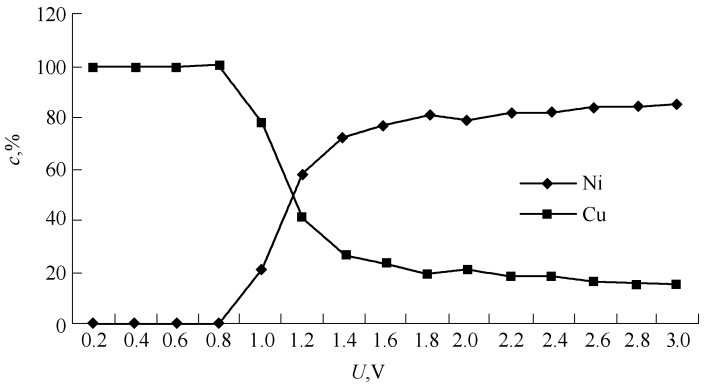


Fig.2 Graphs of the dependence of the composition of the sample (Ni and Cu) on the growth voltage

It follows from Fig. 2 that the optimal potential for copper deposition is 0.8 V, and the optimum potential for Ni deposition is 1.8 V. With further increase in the potential, the Ni concentration with respect to Cu varies insignificantly, but the surface has a more loose structure and more irregularities.

3 Obtaining and researching nanowires

Based on the above results, the first sample of multilayer nanowires was obtained. At this stage, deposition was already carried out in the pores of track matrices with a pore diameter of 100 nm. The matrices were industrial track membranes obtained by irradiating a polymer film with heavy high-energy ions at an accelerator. On the surface of the track membranes, a copper layer 5-20 nm in thickness was deposited previously by the method of thermal sputtering in vacuum, which was then grown by electrolytic deposition. The potential at which the build-up was carried out was 0.6V, and the time was 30 minutes. This made it possible to create a relatively strong conductive substrate for subsequent growth of the TM.

Table 2

Voltage, V	Time of one step	Amount of cycles	Total time
0.8	5 min	3	30 min
1.8	5 min		

The mode of deposition of a sample of multilayer nanowires No. 1 is shown in Table 2.

After electrodeposition, the matrix was dissolved in a 6-normal solution of NaOH in a course of 2 hours at a temperature of 60 ℃, and an array of "free-standing" nanowires was formed. Further, an electron microscopic study of the resulting array was carried out. The general view of the NT array is shown in Fig. 3. Also part of the sample was damaged, in order to place nanowires horizontally (Fig. 4).

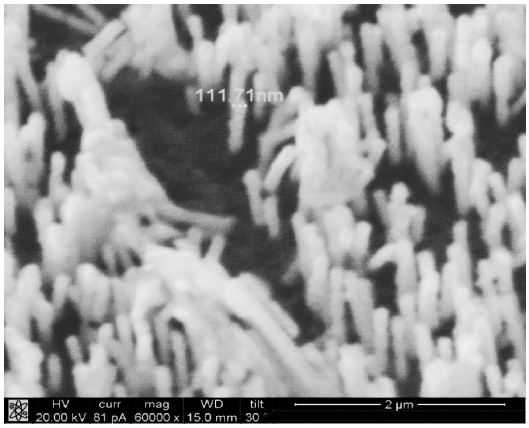


Fig.3　The general view of the array of free-standing nanowires (the diameter of the NP-about 100 nm)

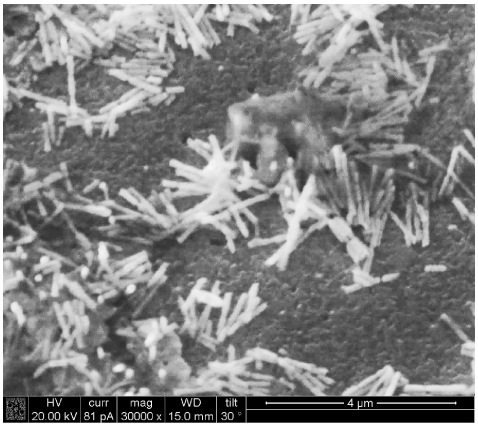


Fig.4　The damaged region of sample No. 1

Fig. 4 clearly shows the differences in the structure of nanowires in the course of its growth. However, these areas turned out to be strongly unequal in size.

To make the layers the same in length, it was necessary to find the times of full filling of the matrix at both chosen potentials. To do this, using the same electrolyte, deposition was carried out without changing the potential, and the current was also fixed with time. When the matrix is completely filled, overgrowths ("caps") begin to form on its surface, which leads to a sharp jump in the strength of the current. On this knob you can accurately determine the growth time of nanowires for each potential. The result of this experiment indicates that the ratio of the Cu / Ni deposition times is approximately equal to 12.5.

In analyzing the results obtained, the main problem was the confirmation of the composition diversity along the length of the nanowire. A special preparation of the sample made it possible to single out a separate group of NWs and to conduct its elemental analysis at various points. The appearance of the group of NWs under study with the number of probe steps is shown in Fig. 5, and the results of elemental analysis at the marked points are given in Table 3.

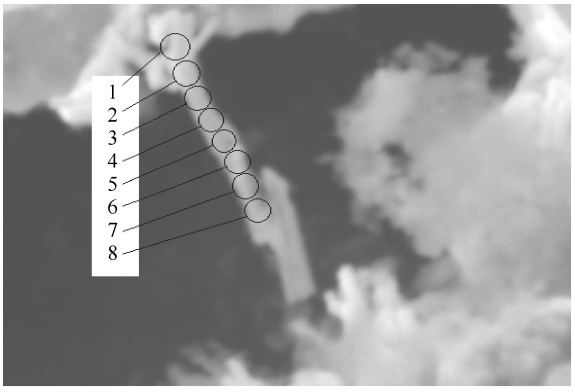


Fig.5　Appearance of the group of research NWs

Table 3

Number of probe step	Element	
	Ni	Cu
1	66.39	33.62
2	78.06	21.95
3	67.7	32.31
4	61.66	38.35
5	54.76	45.25
6	57.85	42.16
7	67.44	32.57
8	77.13	22.88

Using the obtained data, plots of the Ni and Cu concentrations versus the probe pitch were plotted. The results are shown in Fig. 6.

Fig. 6 shows a strong change in the concentration of Ni and Cu, which corresponds to different layers. Which was the main task of the reserch.

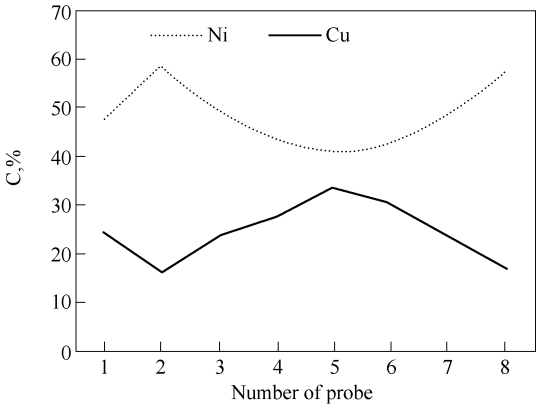


Fig.6 Graph of the dependence of the ratio of Ni/Cu concentrations on the probe pitch

4 Conclusions

At the first stage of the work, the dependence of the composition of the electrolyte-deposited material was studied as a function of the applied voltage. On the basis of the data obtained, the regime of obtaining an array of heterostructural NPs was chosen with the use of a porous matrix-track membrane. The structures obtained are layered nanowires, which is confirmed by the results of electron microscopy. The presence of layers was confirmed by point element analysis on an electron microscope.

Acknowledgements

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