

Structure of Cu/Ni Nanowires Obtained by Matrix Synthesis

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Abstract—The structure of layered Cu/Ni nanowires obtained by template synthesis in 100-nm channels of track membranes has been investigated by transmission and scanning electron microscopy. The phase composition and main structural features of individual nanowires are determined. It is shown that nanowires consist of alternating Ni (*Fm3m*) and Cu (*Fm3m*) layers with grains up to 100 nm in size. It is found that nanowires contain also copper oxide crystallites up to 20 nm in size. The elemental composition of individual layers and their mutual arrangement are determined.

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INTRODUCTION

Fabrication, analysis, and application of nanostructures of different types is one of the main lines of research in science and technology in the last decade [1]. Materials of particular interest include one-dimensional (1D) structures: nanowires, which are used as arrays linked by a common template or base. Ordered arrays of oriented nanowires are obtained by template synthesis [2]. Examples of templates are polymer track membranes, and metals introduced into pores by galvanic deposition method play the role of “filler” [3]. An advantage of this approach is that the nanowire fabrication includes several stages (formation a polymer template, electrodeposition of metals), and the parameters of nanostructures can be varied in each stage [3–5].

The interest in the synthesis of metal nanowires, especially nanowires from magnetic materials, which have been actively developed for the last 20 years [4], is due to the fact that their properties may significantly differ from those of bulk analogs. Several lines of research can be selected in the fabrication of new magnetic nanomaterials. These materials are used in devices with high-density magnetic recording media, based on nanowires made of hard magnetic metals or alloys; screens against electromagnetic radiation, with application of soft magnetic metals and alloys [5]; and sensors with layered nanowires, whose operation is based on the giant magnetoresistance effect [6, 7].

Alternating layers of different materials were obtained as long ago as in the beginning of the XX century [8]. These works began with electrochemical deposition of copper and nickel layers onto a flat surface; however, electrodeposition was later used to form alternating layers of different metals in narrow porous channels. Advantages of this method are its low cost and possibility of fine control of different process parameters [9].

Specific features of the formation of nanowires with alternating nickel and copper layers and some of their physical properties were described, for example, in [10, 11], where it was shown that the properties of layers exhibiting giant magnetoresistance depend on their fabrication technique. Chen et al. [12] showed that the composition, microstructure, and magnetic properties of nanowires deposited into polycarbonate track membranes and consisting of Cu and Ni layers are determined by not only their fabrication technique and geometry but also by the alternation order of ferromagnetic layers.

An analysis of the data in the literature indicates there is practically no information about the structure of layered nanowires. In this context, the purpose of this study was to analyze the structure of layered Cu/Ni nanowires synthesized by electrodeposition in pores of track membranes.

EXPERIMENTAL

Metal nanowires were obtained by electrodeposition of Cu and Ni into pores of track membranes used as templates. We applied commercial track templates with a pore diameter of 100 nm from the Joint Institute for Nuclear Research (Dubna). The pore diameter was chosen proceeding from the optimal conditions for transmission electron microscopy of individual wires.

Metals were deposited from a solution of the following composition: 196.7 g/L $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 6.25 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and 31.6 g/L H_3BO_3 . The copper ion concentration in the solution was maintained low to reduce the amount of copper impurity that is inevitably deposited at the nickel deposition potentials used in experiment [13]. We carried out electrodeposition using a galvanic cell fabricated at the Special Design Bureau of the Institute of Crystallography and a programmable ELINS P-2X source, which makes it possible to change voltage cyclically during electrodeposition; the copper deposition time was 25 and 2 s at nickel deposition potentials of 0.8 and 1.8 V, respectively.

For establish a relationship between the structure and synthesis parameters, we prepared nanowires of different lengths. The nanowire length was determined by the number of deposition cycles; one nickel layer and one copper layer were deposited in each cycle.

After depositing nanowires, the growth polymer template was removed. Note that the standard technique of template removal (dissolution in hot alkali) led to partial degradation of nanowires, and they were coated by an amorphous film. For exclude these effects, nanowires were preliminary exposed to 310-nm UV light for 50 h. The illumination led to partial destruction of polymer, as a result of which the alkali etching time of the polymer mask could be reduced, and the etching temperature could be lowered to room temperature.

Structural studies were performed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), electron diffraction, and energy-dispersive analysis (FEI Tecnai Osiris microscope, accelerating voltage of 200 kV). Elemental analysis was carried out using a special SuperX EDS system equipped with four silicon detectors, whose design makes it possible to construct rapidly (for few minutes) large-area distribution maps of chemical elements. The images and electron diffraction patterns obtained in the electron microscope were processed and analyzed using the Digital Micrograph, Esprit, TIA, and JEMS programs.

RESULTS AND DISCUSSION

Galvanic deposition of Cu/Ni-nanowire arrays was performed in the standard mode and controlled using

time dependences of current. Samples of three types with different numbers of voltage variation cycles (10, 20, and 50) and, correspondingly, the same numbers of unit pairs composing individual nanowires were prepared for structural analysis.

Figure 1 shows a SEM image of Cu/Ni nanowires synthesized in channels of track membranes after the membrane removal. The SEM images of all nanowire samples indicate that they do not retain vertical orientation with respect to the substrate. According to the SEM data, the average lengths of the nanowires composed of 10, 20, and 50 pairs of layers (units) are, respectively, 1.54 μm (Fig. 1a), 2.6 μm (Fig. 1b), and 4.75 μm (Fig. 1c). A comparison of the obtained data on the average length of nanowires having different numbers of layers indicates that they grow with different rates when pores are filled during electrodeposition. In the opposite case, the nanowire length would be directly proportional to the number of layers; i.e., the lengths of nanowires consisting of 10 and 20 pairs of layers would differ by a factor of about 2. For all the samples under study, the nanowire diameter remained constant during growth (Fig. 1d).

The grain structure of synthesized nanowires can clearly be seen in TEM micrographs of their fragments (Fig. 2). The contrast in bright-field TEM images (Fig. 2a) indicates that the nanowires are polycrystalline. To study the morphology of grains and identify the phase composition of nanowires, we performed a dark-field TEM and diffraction analysis of their individual fragments (Figs. 2b–2e). Crystallites of different sizes were observed: small (5–20 nm, Figs. 2b and 2c) and relatively large (to 100 nm, Figs. 2d and 2e).

An analysis of interplanar spacings in diffraction patterns revealed that they correspond to several phases. Large bright reflections are mainly due to metals, Ni ($Fm\bar{3}m$) and Cu ($Fm\bar{3}m$), while diffuse rings and small reflections are generally related to copper oxides of different stoichiometry: Cu_2O and CuO . In addition, one cannot completely exclude the presence of Ni oxides with NiO and Ni_2O_3 stoichiometries. They are difficult to identify because of the superposition of lines from different phases. Thus, the character of electron diffraction patterns and their comparison with dark-field TEM images indicate that metal phases are mainly presented by large grains, while crystals of oxide phases are smaller.

An analysis of HRTEM images and the corresponding Fourier diffraction patterns revealed the presence of Cu_2O crystals, which are located in the peripheral parts of nanowires and coated by a thin amorphous shell. An HRTEM image and the corresponding Fourier diffraction pattern of a Cu_2O crystal about 20 nm in size is presented in Fig. 3.

An elemental analysis (construction of distribution maps for chemical elements) confirmed the presence of alternating Ni and Cu layers in all nanowires under study, with any number of layers. However, the mutual

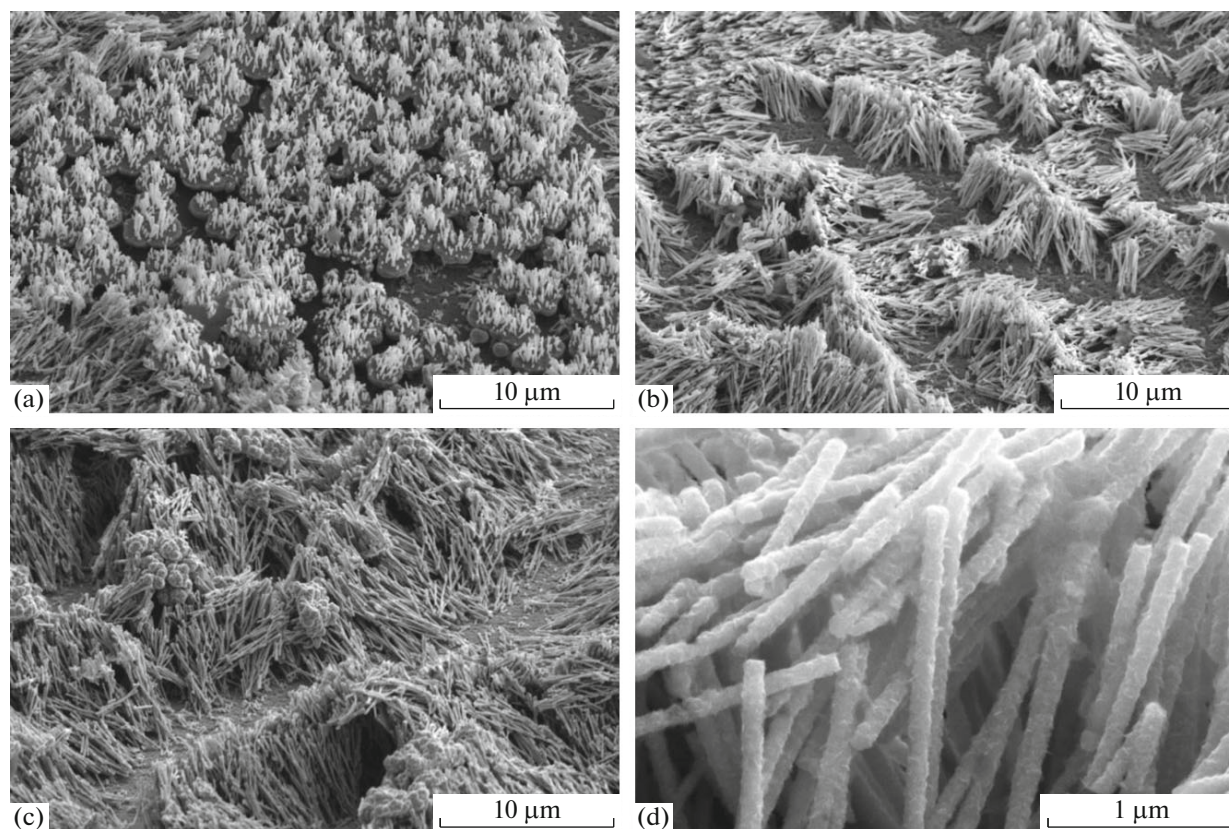


Fig. 1. SEM images of Cu/Ni nanowire arrays synthesized in track membrane channels, after membrane removal: (a) 10, (b) 20, and (c) 50 cycles; (d) enlarged image of individual nanowires synthesized in 50 cycles.

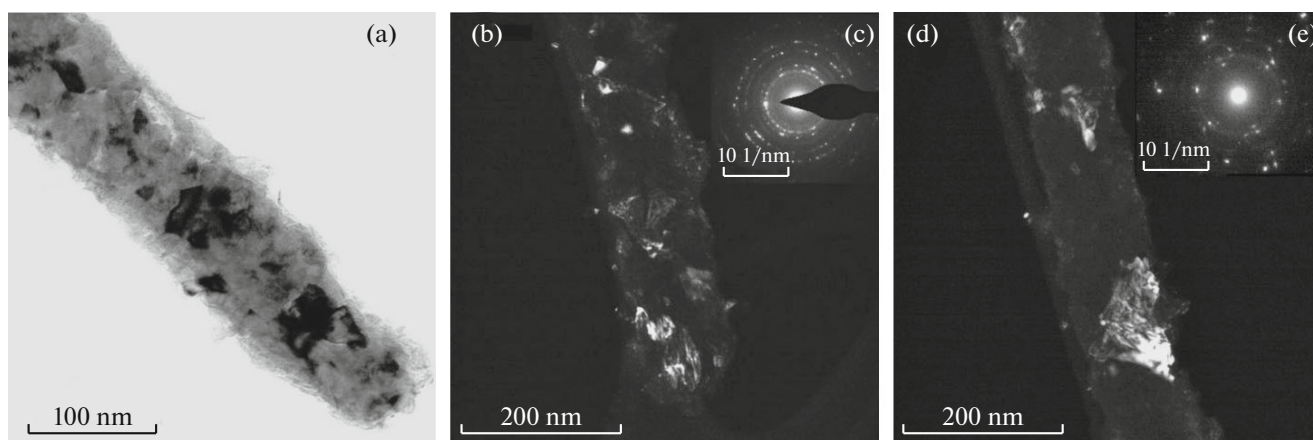


Fig. 2. Structure of individual nanowire (20 pairs of layers): (a) bright-field image of grains, (b, c) dark-field image of small crystals and the corresponding electron diffraction pattern, and (d, e) image of an individual large grain and the corresponding electron diffraction pattern.

arrangement of layers may differ. Ni and Cu layers in the same nanowire may be oriented perpendicular to its axis or make some angle with it (Fig. 4). The thickness of individual units in short nanowires (10 pairs of layers) is mainly in the range of 50–100 nm.

The units of the same nanowire may have different thicknesses. Note that the thickness changes gradually from unit to unit. In Fig. 5, the thickness of layers in long nanowires (composed of 50 pairs of layers) changes from 50 to 400 nm. A likely reason is the

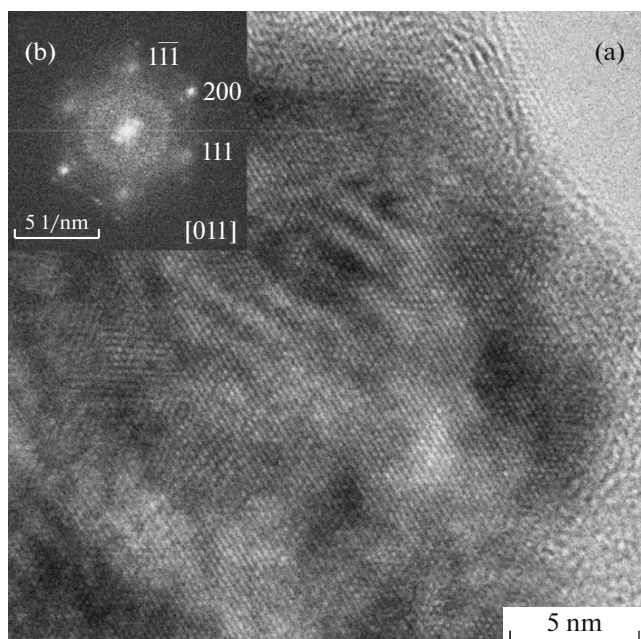


Fig. 3. (a) HRTEM image of Cu_2O crystal and (b) the corresponding Fourier diffraction pattern; [011] zone axis.

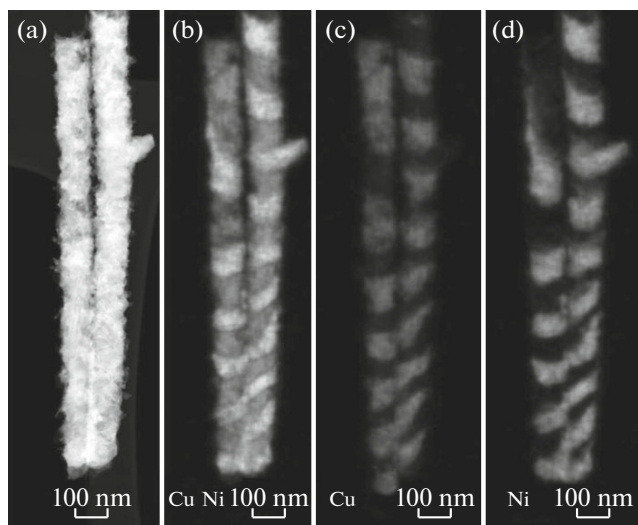


Fig. 4. Arrangement of layers in a nanowire (10 pairs of layers): (a) STEM image with z -contrast and (b–d) distribution maps of chemical elements.

change in the growth conditions: while a growing nanowire approaches the pore mouth, the length of the pore part that remains unfilled decreases, which leads to an increase in current; enhancement of deposition rate; and, as a result, an increase in the deposited layer thickness. The change in the thickness ratio may also be due to the difference in the diffusion mobilities of ions of different metals. This circumstance explains the nonlinear relationship between the

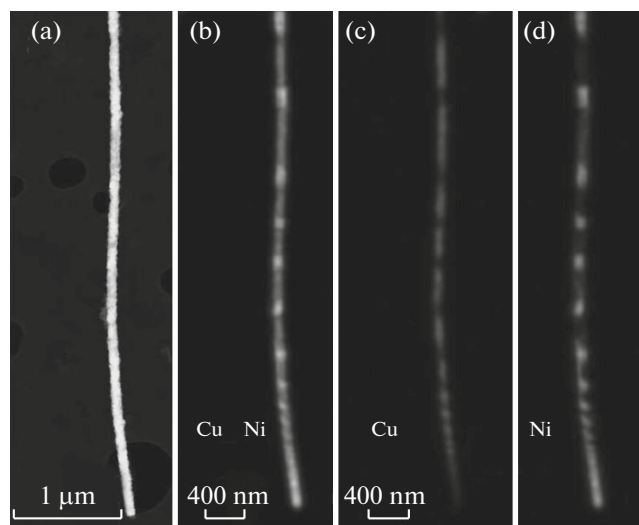


Fig. 5. Fragment of a nanowire (50 pairs of layers) with layers of different thicknesses: (a) STEM image with z -contrast and (b–d) distribution maps of chemical elements.

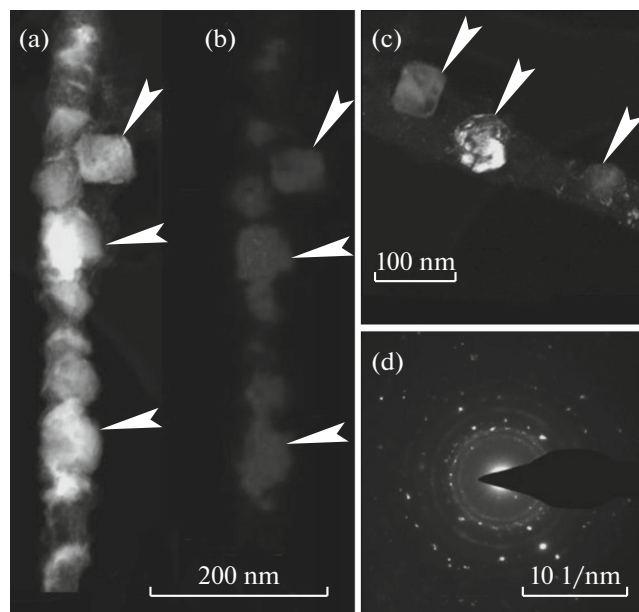


Fig. 6. Fragment of a nanowire with single-crystal units: (a) STEM image with z -contrast, (b) Cu distribution map, (c) dark-field image of single-crystal units, and (d) diffraction pattern from the region shown in (c). Arrows in panels (a–c) indicate the location of Cu crystals whose images were obtained in different microscope operation modes.

nanowire length and the number layers found by the SEM method.

In some cases, units (layers) can be single-crystal. This generally holds true for copper layers. In Fig. 6, arrows indicate single-crystal copper units in the STEM image corresponding to the element distribution map and in the dark-field image of the same

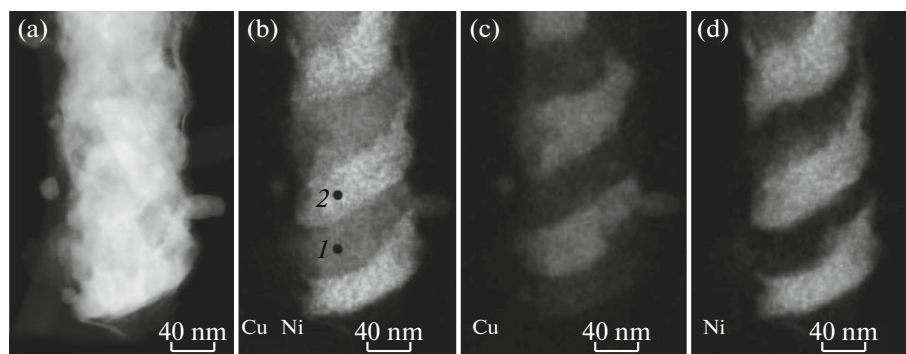


Fig. 7. Image of individual nanowire units (10 pairs of layers): (a) STEM image with z -contrast and (b–d) distribution maps of chemical elements. Numbers 1 and 2 denote the layers for which quantitative energy-dispersive analysis was performed. The elemental compositions of the layers are (1) 97.6 at % Cu, 2.4 at % Ni and (2) 20.1 at % Cu, 79.9 at % Ni.

region of nanowire. A comparison of the maps and dark-field images confirms that these units are Cu single crystals.

An energy-dispersive analysis of the quantitative composition of individual units showed the following: copper units consist mainly of copper, while nickel is almost absent. Nickel units, on the contrary, always contain some amount of copper. This amount may sometimes reach 20%, as confirmed by the data in Fig. 7. The obtained results on the layer composition are in good agreement with the conclusions of [13].

CONCLUSIONS

The structure and phase composition of nanowires consisting of Ni and Cu layers, synthesized in channels of track membranes by electrodeposition, were investigated by TEM, SEM, electron diffraction, and energy-dispersive analysis. The number of pairs of layers in the nanowires was found to be 10, 20, or 50, in correspondence with the number of electrodeposition cycles.

It was shown that the nanowires have a constant diameter of 100 nm along the entire length and consist of alternating Ni ($Fm\bar{3}m$) and Cu ($Fm\bar{3}m$) layers. The size of individual Ni and Cu grains may reach 100 nm; i.e., some units have a single-crystal structure. It was established that, along with metals, nanowires have inclusions of Cu_2O and CuO oxide phases from 5 to 20 nm in size in their composition.

The following features of nanowire layer geometry were found:

(i) layers may be oriented perpendicular to the nanowire axis or make some angle with it;

(ii) the layer thickness lies mainly in the range of 50–100 nm; in some cases it may gradually change along the nanowire length, which indicates a change in the growth conditions during electrodeposition of metals into track membrane pores.

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