Microscopy investigation of conical and layered nanowires

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Abstract. This article discusses the use of scanning microscopy in the study of one-dimensional nanostructures – nanowires. The nanowires were produced by matrix synthesis. Atomic force microscopy (AFM) of conical nanowires was carried out, and layered nanowires were investigated by AFM and magnetic force microscopy (MFM) methods.

1. Introduction
Matrix synthesis is one of the promising methods for producing one-dimensional structures – nanowires (NWs). Track etched membrane (TM) is one of the most popular matrices [1, 2]. This method includes many advantages – the ability to adjust many parameters of both the matrix itself and the deposition conditions. Under certain conditions of etching of the TM, cone-shaped pores can be achieved [3]. At the certain electrolyte and deposition conditions it is possible to obtain a layered structure [4]. This work is devoted to the study of various structures using the methods of electron and probe microscopies.

This paper is devoted to production of conical-shaped nanostructures and their microscopy study, in particular, obtaining a nanocone with a small radius of curvature. Another part of the work is devoted to the production and study of layered NWs. Such NWs consist of alternating layers of magnetic and non-magnetic materials. Magnetic force microscopy (MFM) with application of an external magnetic field was used.

2. Experiment
Typically, TM is produced via etching of irradiated polyethylene terephthalate (PET) film in alkali. In normal mode, the rate of etching of the latent track is much higher than that of the undamaged polymer. As a result, a pore channel of almost cylindrical shape is formed during etching. However, when ethyl alcohol is added to the etcher, the etching rate of the latent track decreases, while that of the intact polymer increases. This makes it possible to obtain a cone-shaped cavity with a certain angle at the top by regulating etching parameters, such as the concentration of ethyl alcohol, etching time, temperature, etc. In this paper, to obtain conical-shaped pores, the irradiated film was etched in a two-normal solution of NaOH alkali with the addition of ethyl alcohol. The studied sample represented irradiated film of PET with the density of the pores 4*10⁷ cm⁻². Three concentrations of ethyl alcohol were used – 25%, 50%, 75%. In addition, etching was carried out at different temperatures – from 10°C to 60°C and durations – from 5 to 60 minutes. The films were etched on both sides. Based on the results of studies
by scanning electron microscopy (SEM) and scanning probe microscopy (SPM), the conditions for producing templates of a certain conical shape were determined.

For a contact layer creation, the surface of the matrices was metallized with a thin layer (about 30 nm) of copper using the method of thermal spraying. For the subsequent production of nanostructures-replicas of pore channels, the method of galvanic deposition of the required metal was used. Thus, the electrolyte of the following composition was used: \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \ 200 \text{ g/l}, \text{H}_2\text{SO}_4 \ 16 \text{ g/l}. \) Moreover, in order to improve the quality of replicas, a brilliant additive CCN-74 in the amount of 5 g/l was added to this composition.

The prepared matrix with a pore diameter of 100 nm and a surface density of \( 1.1 \times 10^8 \text{ cm}^{-2} \) was used to obtain layered NWs. A single-bath method was chosen to obtain these structures. The following electrolyte composition was used: \( \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \ - 197 \text{ g/l}; \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \ - 6.25 \text{ g/l}; \text{H}_3\text{BO}_3 \ - 31.6 \text{ g/l}. \) The deposition was carried out in a special galvanic cell, using the Ellins potentiostat as a source, which allowed to work both in the constant voltage mode and in the "pulse voltage" mode. The mode was selected in such a way that the layers were 100 and 250 nm thick. After the growth, NWs were released from the matrix, and then placed on a flat surface. The samples were covered with a thin layer of copper to prevent oxidation. MFM measurements were carried out using microscope Solver P47-PRO with Multi 75MG probes (BudgetSensor). During the experiment, an external magnetic field directed along the NW with an intensity of 16 mT was applied.

AFM measurements of conical NWs were carried out using microscope Solver P47. Electron microscopy of both conical and layered NWs was performed using a scanning electron microscope JCM-6000plus.

3. Results

3.1. Conical NWs

Analysis of the results allows us to conclude that the angle at the top of the cone depends on the conditions for obtaining a conical pore. So, to increase the angle, you should increase the concentration of alcohol in the etching solution. The same effect is achieved by reducing the temperature of the etching process. Examples of cone structures with "large" and "small" angles at the top are shown in Figure 1. One of the problems of obtaining "sharp" cones is "smoothing" the angle at the top. Obviously, this is due to insufficient electrolyte filling of the top of the pores due to poor wettability. SEM and AFM images of replicas of cone-shaped pores are presented below (Figure 1).

![Figure 1. SEM images of replicas of cone-shaped pores obtained in different conditions: (a) 75% concentration of alcohol, time of etching – 20 min, 20°C; (b) 50% concentration of alcohol, time of etching – 10 min, 40°C.](image-url)
There can be seen a good match between SEM and AFM images. However, there is the rounded, smoothed angle at the top. To overcome this effect, several wetting agents have been tested. The best results were demonstrated by so-called bishopatallah supplements CCN-74.

It is shown that the use of this additive improves the adhesion of the electrolyte to the pore walls, so that NWs have a more elongated shape: the structures shown in Figure b are obtained using CCN-74.

3.2. Layered NWs

A preliminary study was conducted using SEM (Fig. 3). It is shown that NWs completely fill the pores of the matrix, and their diameter corresponds to the pore diameter. TEM microscopy (previously performed in [5] for Ni/Cu nanowires) made it possible to determine the thickness of alternating layers (from 30 to 250 Nm). Elemental analysis showed that alternating layers consisted of pure copper and Nickel-copper alloy (up to 20% copper). To prepare the samples, an aqueous suspension of NWs was applied to the holder by the "irrigation" method with subsequent drying and then covered with a thin layer of metal (by thermal spraying). For MFM measurements, the one-pass technique was used in order to avoid the influence of neighbouring NWs on each other.

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Figure 2. (a) SEM and (b) AFM of conical nanostructures.

Figure 3. (a) SEM and (b) TEM of layered NWs. Layers of Cu and Ni.
Figure 4. (a) AFM and (b, c) MFM images of layered Co/Cu nanowire. (b) without external magnetic field, (c) with external magnetic field of 16 mT. Period of layers is 500 nm.

Figure 5. (a) AFM and (b, c) MFM images of layered Ni/Cu nanowire. (b) without external magnetic field, (c) with external magnetic field of 16 mT. Period of layers is 200 nm.

Figure 4a shows the AFM images of the topography of a single layer Co/Cu NW, Figure 4b shows the MFM image of the same NW, and Figure 4c shows the MFM image after an external magnetic field 16 mT was applied along the NW axis.

It is clearly seen that the NW has a layered structure with a period of about 500 nm, which corresponds to expectations, and it is also seen that the application of the magnetic field along the NW axis leads to the magnetization reversal of the nanowires.

Figure 5 represents the same AFM and MFM study for layered Ni/Cu NW. Period of layers is 200 nm. It can be seen also that external magnetic field affects magnetic state, but layers are not clearly visible.

4. Conclusion
In this work, arrays of conical and layered nanowires were obtained and the study by SEM and AFM was carried out.

It is shown that an increase in the concentration of alcohol and/or a decrease in temperature leads to an increase in the angle at the top of the cone.

An effect of smoothing peaks because of insufficient electrolyte wetting the top of the pores is revealed. Using brilliant additive CCN-74 reduces this effect.

It is shown that by alternating the growth potential in a two-component electrolyte, it is possible to obtain NWs with alternating layers. The correlation of topography and magnetic structure of layered NW is shown by AFM and MFM methods.

A method for fixing NW on a substrate is proposed and it is shown that the application of a small external magnetic field (16 mT) leads to the magnetization reversal of a single NW.
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