Features of electrochemical formation of metal and semiconductor nanowires in anodic alumina matrices with variable pores

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Abstract

Methods for the porous membranes formation from anodic alumina with periodically alternating pore diameters along the membrane depth and the electrochemical nanowires formation of complex morphology from various materials have been developed and tested. The features of the electrochemical deposition of indium and copper antimonide into pores with varying diameters under different chemical conditions and electrical modes have been investigated. The electron microscopic studies of the created nanosystems have been carried out, the elemental composition has been investigated, the current-voltage characteristics of InSb nanowires of complex morphology have been measured.

Keywords: porous anodic alumina oxide, variable pores, electrochemical deposition, semiconductors, nanowires.

Introduction

Inasmuch as quantum laws operate at the nanoscale, any change in the composition or geometry of a nanoobject can lead to a fundamental change in the physical and chemical properties of the entire structure [1]. This necessitates the creation of more complex structures (nanotubes and nanowires with different diameters at different heights, with branching, etc.). This result can be achieved by means of electrochemical template synthesis of nanostructures in porous matrices with complex nanopore geometry [2, 3]. Of particular interest are nanostructures with periodically varying pore diameters from the surface to the base.

This article presents the series of laboratory experiments in which the technology of creating anodic aluminum oxide matrices with alternating pore diameters has been worked out. Such a matrix consists of several layers of adjustable depth with specific pore diameters along the entire height of these layers and was used as template for electrochemical deposition of metal and semiconductor nanowires.

Experimental

An anodic alumina (AA) membrane with alternating pore diameters was formed by anodizing aluminum foil (99.999%) and contained four layers 10 μm thick with alternating pore diameters. The anodizing voltage determined the pore diameter, as well as other geometric parameters of the pores, which was set during the growth of the AA layer. Since one electrolyte is suitable for anodizing in a narrow voltage range, separate electrolytes were made for different layers, which were replaced at the junctions between the layers. As a result, transitions between 120 V (malonic acid 0.4 M) and 40 V (oxalic acid 0.3 M) were realized. The first and third layers were formed at a constant voltage of 120 V, and the second and fourth at a constant voltage of 40 V. For the transition from larger pore diameter to smaller one, the current was limited to 1 mA/cm^2. As a result, the voltage gradually decreased to stationary value, which was approximately 93 V at such current density in the solution of 0.4 M malonic acid. After replacing the electrolyte, the voltage grew up to the previous level (93 V), and then decreased and was set at the level of the operating voltage of the second electrolyte (40 V). The transition from smaller pore diameter to larger one was formed directly by replacing the second electrolyte with the first one at the very beginning of the transition. In this case, for smoother voltage sweep, the current limit was also fixed at 1 mA/cm^2, the operating voltage rose to 120 V and stabilized, while the anode current increased to a stationary level.

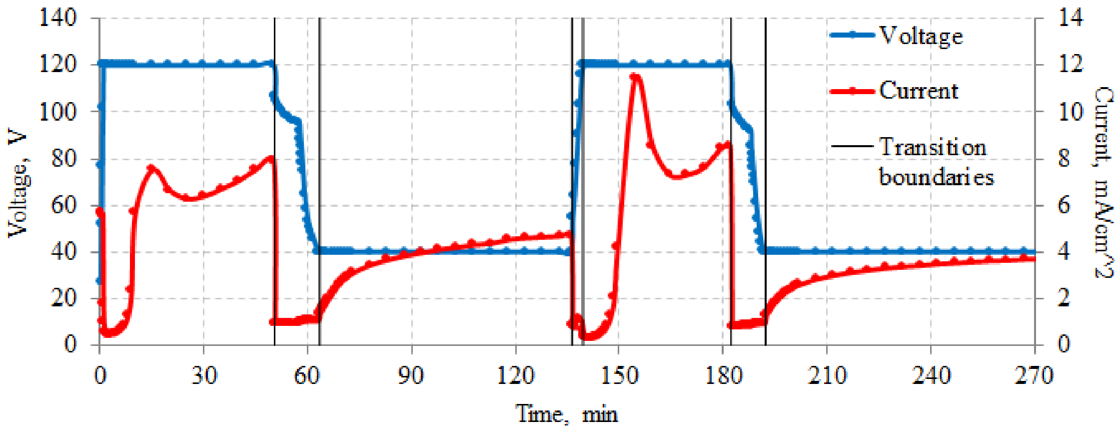


Figure 1. Kinetic dependences of voltage and anode current during the membrane preparation with variable porosity

After completion of the porous structure formation, selective etching of the remaining aluminum in $CuCl_2$/HCl solution and a barrier layer (BL) in 10% orthophosphoric acid solution (at 35°C) was carried out. The etching time of BL was determined basing on its thickness h_{BL}=1.2U(nm). The etching rate of the BL layer was determined by the formula (nm/min):

$$r = e^{29,31-\frac{8816,3}{273+T}}$$

For the BL confident dissolution, the etching time was increased by 2-3 minutes.

For the deposition of metals and semiconductors into the pores, an electrical contact is required at the pores bottom; therefore, the membrane preparation technology has been slightly changed. Four layers of anodic oxide, 10 µm each, were formed on an aluminum foil with alternating voltages of 120 V (malonic acid 0.4 M) and 50 V (oxalic acid 0.3 M). Then, a layer of copper with a thickness of 2 µm was applied to the upper surface of the membrane by magnetron sputtering, then it was masked with varnish, and the aluminum was successively removed and the BL was dissolved according to the previously described method. The electrochemical deposition of Cu into variable pores along the entire depth was carried out from the solution of 0.5 M $CuSO_4$, 0.1 M H_2SO_4 at an anodic current density of about 2 mA/cm^2, while the voltage was 1.05-1.1 V. Figure 2 (a) shows the kinetic dependences current and voltage when the filling anodic alumina membranes with alternating pores. When the deposited copper began to protrude to the surface, the process was stopped.

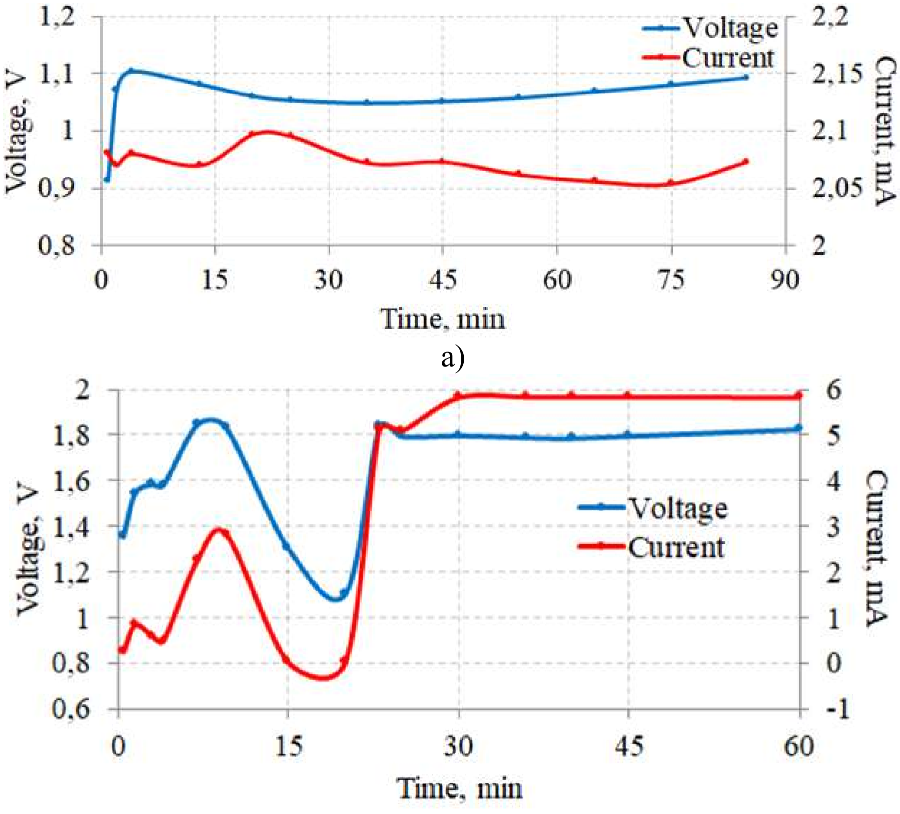


Figure 2. Kinetic dependences of current and voltage when filling with copper (a) and InSb (b) of anodic alumina with alternating pores

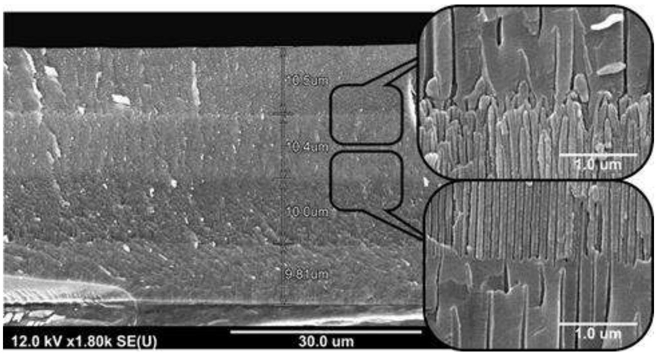
Electrochemical deposition of a semiconductor compound InSb was carried out from a solution containing 0.1 M $SbCl_3$, 0.15 M $InCl_3$, 0.36 M citric acid, 0.17 M potassium citrate and 0.1 g of surfactant. The kinetics of deposition is shown in Figure 2(b). The process was stopped after the release of InSb from the pores to the surface of the sample.

Current-voltage characteristics were measured using a specialized probe device connected to the InSb on the surface and to the copper sublayer. Electric modes were set with a stepwise increase in voltage from -6 to 6 V using a Keysight 34401 source, the current-voltage characteristics were recorded using a Keysight B2901A parametric analyzer, and the measurement process was controlled using a USB interface in the EasyEXPERT group + software environment.

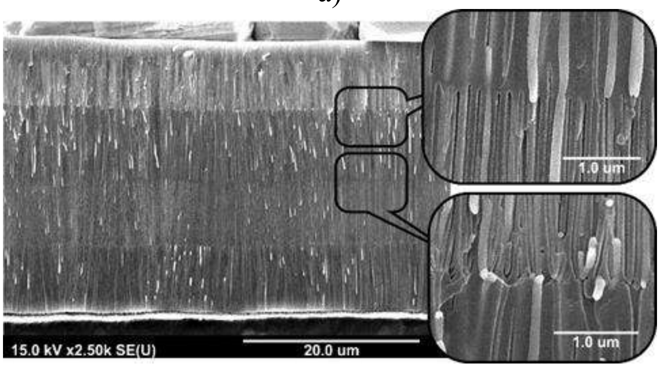
Results and discussion

Figure 3(a) shows electron microscopic images of the formed membrane cross-sections. The images clearly show layers of porous anodic alumina with different pore diameters. The inserts show the transitions and branching of pores from the larger size to the smaller one (on high) and sealing when moving from the smaller size to the larger one (at the bottom). Presumably, competition for the charge passing through them leads to the preferential sealing, rather than the unification of most of the pores. This is a significant problem for filling such a structure with metal by the electrochemical deposition, since the pores sealed even on one side are not electrically connected either with the contact or with the electrolyte and, as a result, are not filled.

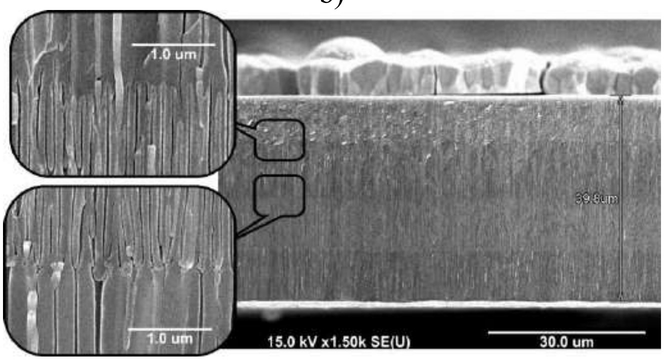
Figure 3 (b) demonstrates significant filling of Cu pores along the entire height. Close-up images show how Cu overcomes the transitions and branches out in places in accordance with the pore configuration. Probably, in a quantitative ratio, wide and narrow pores are filled approximately in the same way, but as a percentage, narrow pores are filled less often. This observation confirms the fact that the branches sealed on one side do not create an electrical circuit and, as a result, do not fill.



a)



b)



c)

Figure 3. Cross-section of the sample and its transitions from larger pore diameter to smaller (top) and from smaller to larger (bottom) (a); AA matrix with deposited copper nanowires from larger pore diameter to smaller one (insert from above) and from smaller one to larger one (insert from below); AA matrix with deposited InSb

The filling of the pores with indium antimonide from the bottom of the matrix to the surface is not the same, so the cations, when moving through the branched pores, encounter difficulties in overcoming each transition between the branching pores, not all are uniformly filled. However, as can be seen from Figure 3 (c), InSb is capable of overcoming transitions and branching in accordance with the pore configuration during deposition. On the kinetics of InSb deposition on the

(Figure 2 (b)), synchronous fluctuations of the voltage and current density values were observed, which can be associated with a change in the working area during the transition between the layers. Such current surges lead to a change in the deposition rate and uniformity of pore filling.

The current-voltage characteristics of indium antimonide nanowires, shown in Fig. 4, showed that the right branch of the I-V characteristic of the InSb structure represents the beginning of the I-V characteristic of a typical semiconductor, that is, the beginning of a parabola. In this case, the shape of the forward branch of I-V characteristic does not differ from the reverse one. This means that a complex InSb nanostructure of this kind does not yet possess either special electrical properties or the property of current rectification. Nevertheless, it can be noted that the I-V characteristic of the structure is reproducible at different points. In the future, accurate modeling of a complex structure and its properties (such as the number of layers, their sequence, thickness, etc.) can make it possible to create a structure with properties promising for practical application.

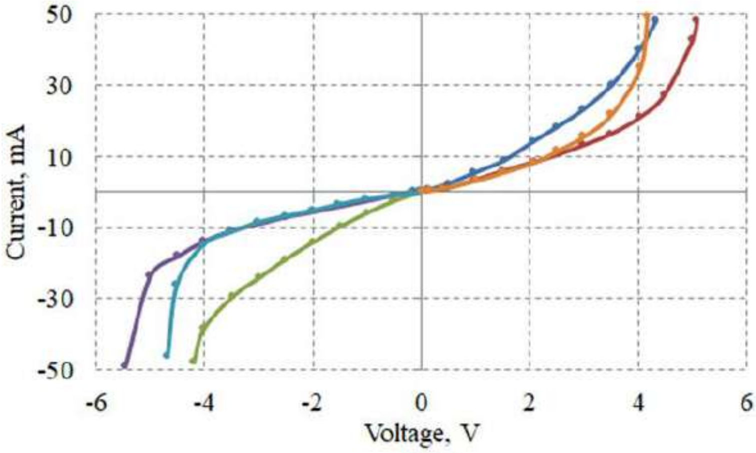


Figure 4. I-V characteristics of InSb nanowires with variable pore diameters

Conclusion

Techniques for the formation of nanoporous membranes from anodic alumina with alternating pore sizes have been developed and investigated, and are adapted for the deposition of metals and semiconductors. Manufactured membranes were tested in the electrochemical deposition of copper and indium antimonide. Electron microscopic studies of the formed nanosystems have been carried out and a pore filling mechanism has been proposed. The current-voltage characteristics of arrays of nanowires with a variable diameter are investigated. The data obtained make it possible to determine the technological parameters in order to reproduce and controllably obtain arrays of nanowires with variable morphology.

Acknowledgment

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References:

[1] G.G. Gorokh [et al.] Techn. and design in electronic equipment. 1 (2015) 3–12.
[2] G.G. Gorokh [et al.] Semiconductors. 51 (2017) 850–853.
[3] I.A. Obukhov [et al.] Nanoindustry. 77 (2017) 96–108.