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Abstract. The processes of synthesis ordered nanowire arrays of bismuth in anodic alumina template ware developed. The sequence of technological operations for the formation of porous templates for the electrochemical deposition of nanowires was described. Optimum electrochemical conditions of reproducible synthesis uniform nanowire arrays were determined. The microstructure and composition of formed structures was studied. The developed techniques are effective for creating perspective nanostructures used in thermoelectric devices.

1. Introduction

At present, alternative sources of energy, such as solar energy, biofuel, wind power, as well as thermal converters, become more relevant. Especially promising is the development of thermoelectric converters of unused industrial heat directly into electrical energy. From a practical point of view, the most important parameter determining the properties of the thermoelectric material is thermoelectric figure of merit $ZT = \sigma S^2 T/k$ where σ, S, and k are the electrical conductivity, the Seebeck coefficient, and the thermal conductivity, respectively. $ZT \geq 3$ - is necessary condition in which it becomes possible to replace the mechanical generators with thermoelectric generators. Nanostructured thermoelectric materials, such as materials with superlattices, systems with quantum wells and dots, quantum wires and nanocomposites can provide high ZT [1-5]. Mathematical model shows, that bismuth nanowires with diameter 5 nm and dopand concentration 10^{18} cm^{-2} provides ZT up to 6.3 [6]. One of the factors affecting the increase in ZT is the additional scattering of phonons at the boundaries of the nanowires, which leads to a decrease in the thermal conductivity [7]. Also, using of porous alumina as a template, that has low thermal conductivity [8], contributes to an increase the thermoelectric figure of merit. In this work we present the technique of creating of nanostructured thermoelectric material based on bismuth nanowires synthesized in porous anodic alumina (PAA) templates.

2. Experimental

The matrices of bismuth nanowires were formed by electrochemical deposition in templates of porous anodic alumina (PAA). The sequence of matrix preparation operations is shown on figure 1. Templates 30 μm thick and with pores diameter of 70 nm were obtained by two-step anodizing of Al foil (99.99%) of 100 μm thickness. A Keysight N5751A power supply was used as the anodizing unit. First stage anodization was carried out in two-electrode electrochemical cell in 0.4 M/dm^{-3} solution oxalic acid at constant applied potential of 55 V (Figure 1, a). As the cathode we used an aluminum plate located parallel to the anodized foil at distance of 10 cm. The electrolyte was intensively agitated by magnetic stirrer RH 2 (IKA) and temperature of electrolyte was kept equal to 10 °C using thermostat. The first stage of anodizing was carried out to a depth of 5 μm. The thickness of the

formed anodic alumina layer was controlled coulometrically. Further 5 μm thick sacrificial alumina layer, formed during first anodization stage, was selectively dissolved in an aqueous solution containing 1.12 M/dm^3 H_3PO_4 and 0.6 M/dm^3 CrO_3 at 75 ± 1 °C for 25 min (Figure 1, b). The second anodization of Al in 0.4 M/dm^3 oxalic acid at 55 V leads to the formation of ordered porous anodic alumina template with hexagonal arrangement of pores (Figure 1, c). A copper layer with thickness of 1 μm was deposited by magnetron sputtering onto one side of the AAO template to serve as cathode for electrochemical deposition of bismuth nanowires (Figure 1, d). Further, a porous anodic alumina layer, a remaining aluminum layer and a barrier oxide layer were successively selectively dissolved (Figure 1, e). A porous alumina layer was selectively dissolved in solution 1.12 M/dm^3 H_3PO_4 and 0.6 M/dm^3 CrO_3 at 75 ± 1 °C for 25 min. Selective removal of remaining aluminum layer was carried out in 0.01 M/dm^3 $CuCl_2$ and 2 M/dm^3 HCl solution at 15 °C during 20 min. The barrier oxide layer on the bottom of PAA templates was removed in 0.5 M/dm^3 solution of orthophosphoric acid during 10 minutes at a temperature of 50 °C with stirring (Figure 1, f). Pore widening operation was carried out in 2 M/dm^3 solution of H_2SO_4 with stirring during 15 minutes at temperature of 50 °C (Figure 1, g). Pore widening is necessary to increase porosity and provide the required pore diameter.

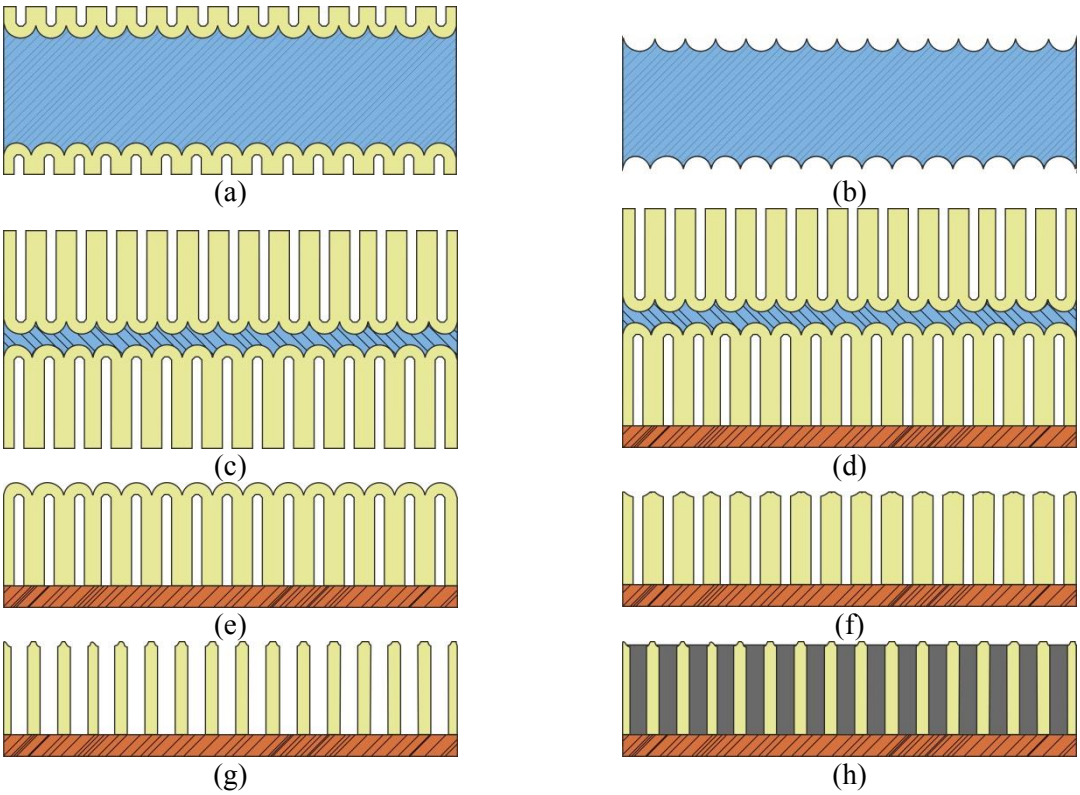


Figure 1. The main phases of the matrices of bismuth nanowires formation process: (a) first stage anodizing of aluminium foil; (b) selective dissolution of sacrificial porous oxide layer; (c) second stage anodizing of structured aluminium foil; (d) magnetron sputtering of copper layer on porous surface; (e) selective dissolution of porous alumina layer and remaining aluminum layer; (f) barrier oxide layer dissolution; (g) pore widening operation; (h) electrochemical deposition of bismuth.

Electrochemical deposition of bismuth into the prepared matrix was carried out in solution consisting of 0.13 M/dm^3 $BiCl_3$, 1.2 M/dm^3 NaCl and 1 M/dm^3 HCl onto copper sublayer, treated with a 0.05 M/dm^3 sulfuric acid during 1 minute at room temperature (Figure 1, h). Cathodic polarization curve was determined during deposition on the copper layer. The curve was determined in the voltage range 0 … -1.2 volts, with a scanning speed of 0.005 V/s and a step of 0.0025 V, in a three-electrode cell with a silver chloride reference electrode. Carbon electrode uses as anode. PGSTAT302N power

supply, connected to a personal computer with the Nova 2.0 software package, was used for the determination of cathodic polarization curves. Deposition into PAA was carried out in the galvanostatic mode at current densities of 10 mA/cm^2, 20 mA/cm^2 and 30 mA/cm^2, which were chosen after analysis of polarization curves. Deposition time was 20 minutes and during electrodeposition the electrolyte was constantly agitated by magnetic stirrer. SEM images of the PAA templates and Bi/PAA nanocomposites were collected using scanning electron microscope of high resolution S-4800 f. Hitachi. A gold layer 5 nm thick was sputtered on the surface of the samples before SEM analysis. An electron probe X-ray spectral microanalysis of electrochemically deposited Bi nanowires in the pores of AOA membranes was carried out on a scanning electron microscope equipped with a special AN 10000 detector from Princeton Gamma-Tech, Inc. This detector registered the characteristic X-ray radiation from all elements that fell under the action of the primary electron beam of the microscope. The spot from the primary ray had a characteristic size of 2 μm. The penetration depth of the beam was from 0.1 μm to several microns.

3. Results and discussion

Structure of PAA templates on different stages of preparation is shown on SEM images (Figure 2). At first stage of anodizing pores nucleate chaotically, mainly on defects in the structure of aluminium (Figure 2, a). During oxidation pores are self-organized and arranged in an ordered hexagonal structure. At second stage of anodizing pores nucleate on pre-patterned metal surface, obtained after the selective dissolution of sacrificial alumina layer. This allow to form porous films with ordered structure (Figure 2, b). After selective dissolution of a porous anodic alumina layer and remaining aluminum layer we obtain a freestanding oxide template with barrier oxide layer and copper layer on another side (Figure 2, c, d). After the local etching of the barrier oxide layer, a pore diameter and porosity was 45 nm and 10% respectively (Figure 2, e, f). Mathematical modelling of thermal conductivity of porous membranes shows, that an increase in porosity of up to 30% leads to a decrease in the thermal conductivity by 30% [8], which can positively affect on the figure of merit of the thermoelectric composite. Thus, the diameter of channels in PAA was widened by etching the received templates, and resulting diameter of pores was 70±2 nm, and porosity about 30% (Figure 2, g, h).

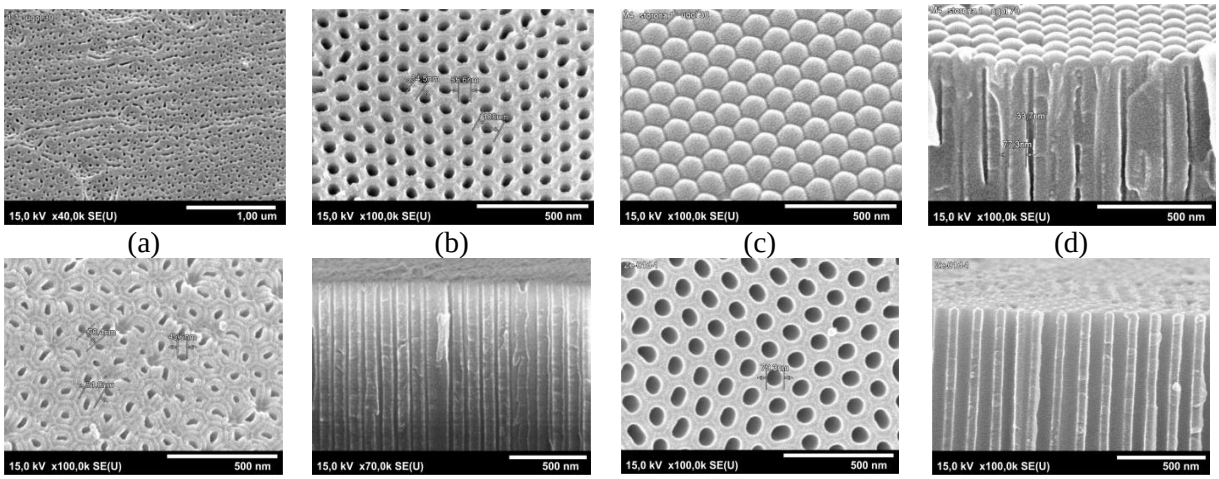


Figure 2. SEM images of anodic alumina templates: (a) surface of alumina foil after first stage of anodizing; (b) ordered surface of porous anodic alumina template after second stage of anodizing; (c, d) barrier oxide layer of porous template; (e, f) surface and cross section of template after barrier oxide layer removal; (g, h) surface and cross section of template with enlarged pores.

The analysis of the polarization curves made it possible to determine the optimal electrical conditions of electrochemical deposition of bismuth nanowires. The polarization curve has three characteristic areas (fig. 3). Area I corresponds to the voltage range at which electrochemical deposition of metal occurs on the copper surface. The maximum current density in the voltage range -0.24 ... -0.31 V (area II) is explained by the limiting ion (Sb^-) diffusion current I_d. When the limiting diffusion current is reached, it sharply deteriorates the quality of the deposited metal. Therefore, the operating range of the metal deposition current densities below 90% of I_d, at voltage range -0,16…-0,24 V and current densities of 5…24 mA/cm^2. Further polarization (area III) leads to an increase the current density due to hydrogen evolution on copper layer, which prevents the formation of bismuth nanowire in the PAA template.

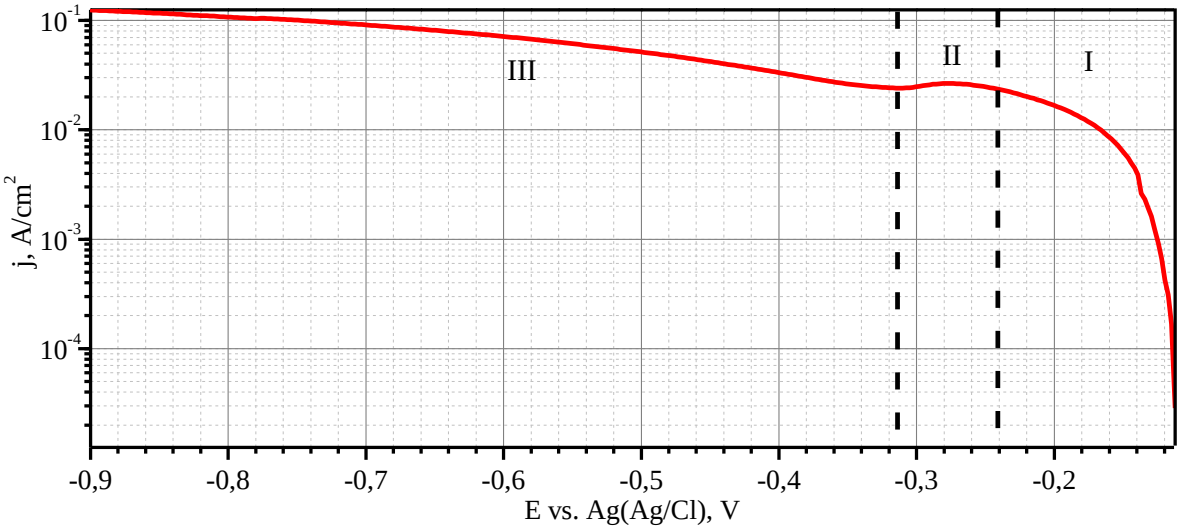
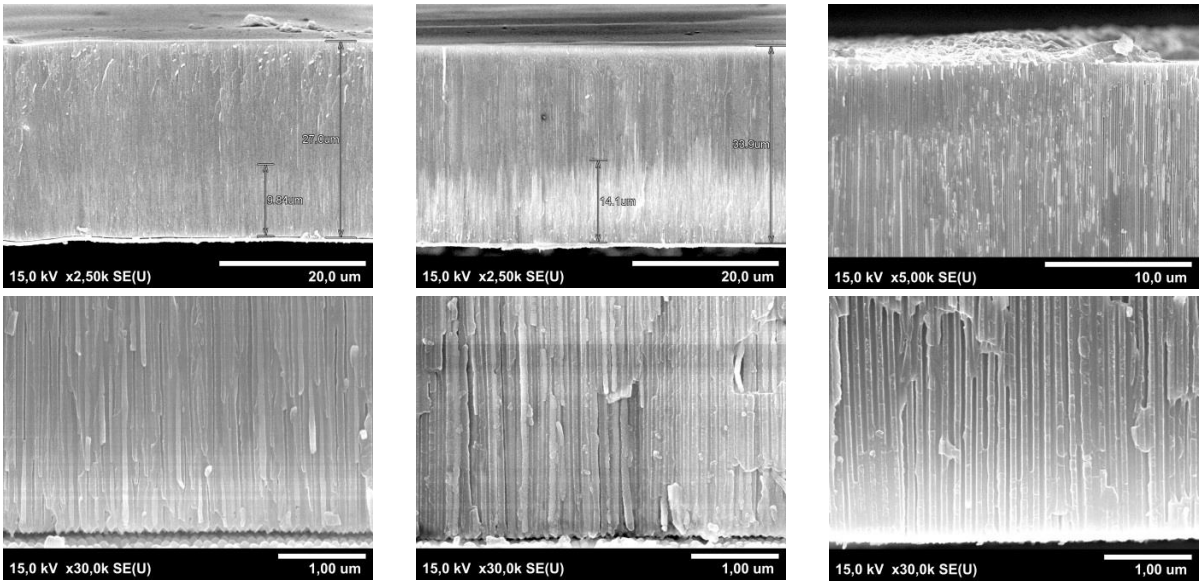


Figure 3. Cathodic polarization curve of porous electrode, based on 30 μm thick PAA template with ordered porous structure and copper sublayer, in solution consisting of 0.13 M/dm^3 $BiCl_3$, 1.2 M/dm^3 NaCl and 1 M/dm^3 HCl. Potential scan rate is 0.005 V per second. The current was normalized on geometric area of the sample (0.8 cm^2)

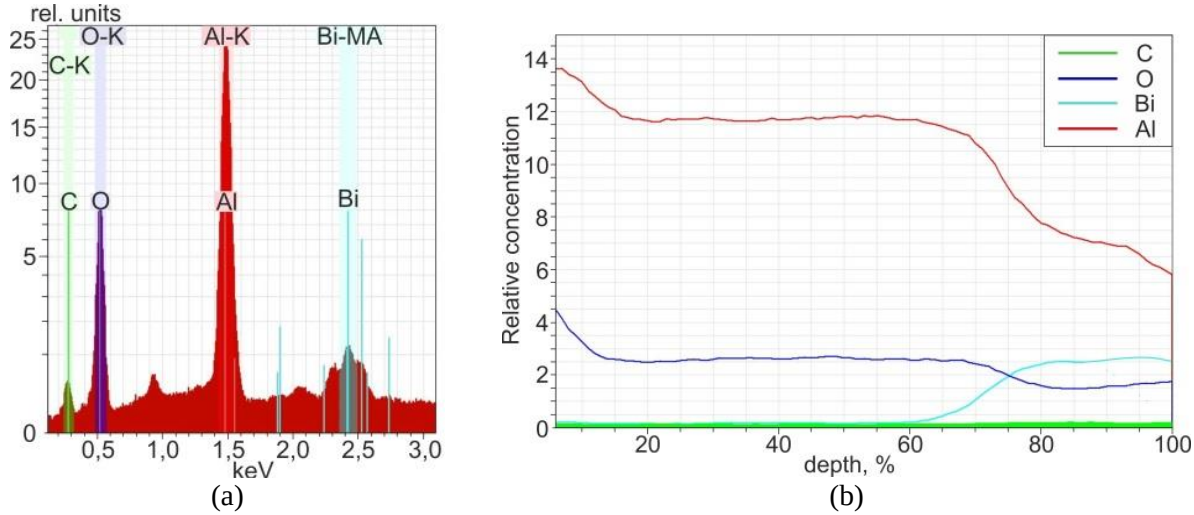
SEM images of templates with deposited bismuth ware analysed (Figure 4). In sample of nanocomposite with bismuth nanowires formed at current density 10 mA/cm^2 (Figure 4, a) PAA template is filled at 9.84 μm. In this electrochemical condition of formation the growth rate of nanowires is 0.492 μm/min. In each pore a nanowire was synthesized with a diameter corresponding to the pore diameter. PAA template with bismuth nanowires formed at current density 20 mA/cm^2 is filled at 14.1 μm, that corresponds to growth rate of 0.705 μm/min (Figure 4, b). The disproportionality of the deposition rate and the current density can be related to a change in the percentage of current efficiency with the current density increase. In sample formed at current density 30 mA/cm^2 (at voltage above -0.24 V) nanowires inside the porous template are not detected (Figure 4, c). This may be due to the intensive evolution of hydrogen on the copper sublayer, which prevents the formation of bismuth nanowires in the pores and deposition occurs on the surface of the membrane. Thus, the most reproducible and uniform electrochemical deposition is carried out at current densities of 10 ... 20 mA/cm^2 with formation bismuth nanowires at each pore with diameters corresponding to pore diameters of 70 nm.



(a) (b) (c)

Figure 4. SEM microphotographs of PAA cross-section with bismuth nanowires formed at different current densities: (a) PAA template with Bi nanowire array 9.84 μm length, deposited at 10 mA/cm^2; (b) (a) PAA template with Bi nanowire array 14,1 μm length, deposited at 20 mA/cm^2; (c) PAA template with layer of bismuth on surface of template, deposited at 30 mA/cm^2.

Figure 5 shows the data of investigations of Bi nanowires composition in the porous PAA template as spectra of electron probe x-ray spectral microanalysis. On the spectrum there are lines corresponding to the elemental composition of the original matrix: the line with maximum of 1.62 keV corresponds to aluminium in the PAA structure, with maximum of 0.51 keV – oxygen. The electrochemically deposited nanowires in the pores is reflected by several lines in the spectrum that corresponds with bismuth in various forms (1.87 keV, 2.52 keV, 2.57 keV and 2.74 keV) with a maximum band of 2.42 keV.



(a) (b)

Figure 5. Spectrum of energy dispersive X-ray spectroscopy of PAA template with bismuth nanowires deposited at current density 20 mA/cm^2 (a) and distribution of elements in depth of nanocomposite (b).

4. Conclusion

The technique of nanoporous templates formation for the electrochemical synthesis of nanowires from semiconductors and semimetals with large aspect ratio of diameter to length has been developed. This method allows by varying the formation conditions to control the pore sizes and their scaling controllably. Nanoporous templates were used to obtain arrays of bismuth nanowires by electrochemical deposition from chloride solutions. As the result of electrochemical synthesis, the bismuth nanowires are formed in each pore, and their diameters correspond to the pore sizes, and length is determined by the duration of deposition. The developed methods make it possible to reproduce nanowires of semimetals with the required physicochemical properties, which opens the prospect for the creation of wide range of thermoelectric devices, such as thermo-generators, microcoolers, as well as devices operating on quantum effects with low production costs. Further work will be aimed at studying the thermoelectric properties of obtained nanocomposites.

Acknowledgments

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References

[1] Boukai A., Xu K., Heath J. R., 2006 Adv. Mater., **18**(7) 864
[2] Ali A., Chen Y., Vasiraju V., Vaddiraju S., 2017 Nanotechnology, **28**(28), 282001.
[3] Gorokh G. G., Lozovenko A.A., Bulat L.P., 2017 Semiconductors, **51(**7), 850
[4] Gorokh G. G., Obuhov I. A., Lozovenko A. A., 2015 TKEA, **1** 3.
[5] Obuhov I. A., Gorokh G. G., Lozovenko A. A., Smirnova E., 2017 Nanoindustry, **6**(77), 96.
[6] Lin Y. M., Sun X., Dresselhaus M. S., 2000. Physical Review B, **62**(7), 4610.
[7] Chen G, Narayanaswamy A., Dames C., 2004. Superlattices And Microstructures, **35** 161.
[8] Belahurau Ya. A., Shukevich Ya. I., Barkalin V. V., Khatko V.V., Taratyn I.A., 2012. Nano- and microsystems technology, **1** 18.