Synthesis of bismuth nanowires for thermoelectric applications

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Abstract. The processes of synthesis ordered nanowire arrays of bismuth in anodic alumina template ware developed. Optimum conditions of electrochemical deposition for uniform and reproducible formation of 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 [1-5], such as materials with superlattices, systems with quantum wells and dots, quantum wires and nanocomposites can provide high ZT. The work shows the technique of creating of nanostructured thermoelectric material based on bismuth nanowires.

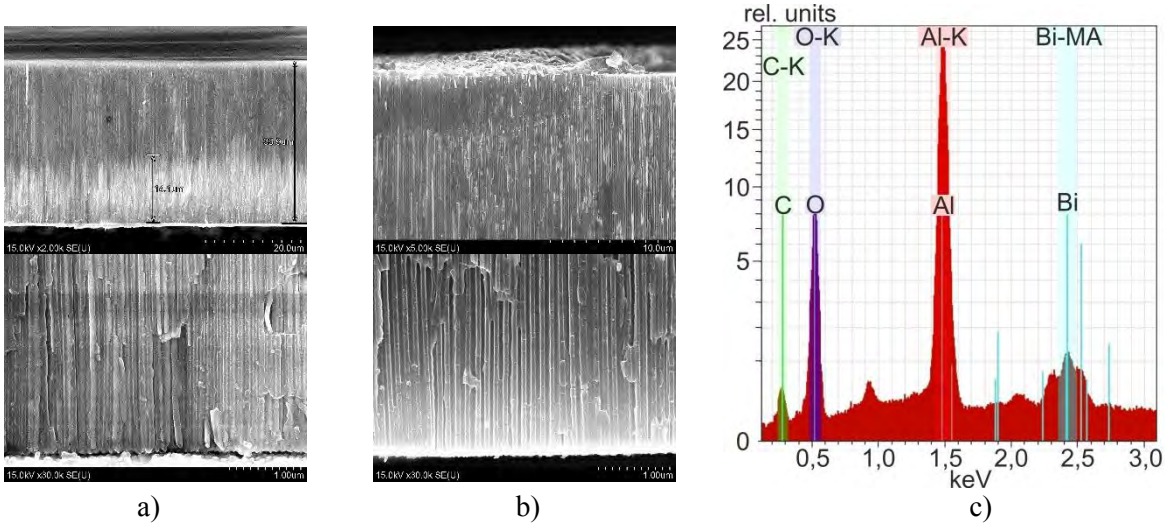
2. Experimental

The matrices of bismuth nanowires were formed by electrochemical deposition in templates of porous anodic alumina (PAA). Templates 30 um thick and with pores diameter of 70 nm were obtained by two-step anodizing of Al foil. A copper layer with thickness of 1 μm was deposited on the porous surface of the anodic alumina to create an electrical contact. 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. 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. Deposition was carried out in the galvanostatic mode at current densities of 10 mA/cm^2, 20 mA/cm^2 and 30 mA/cm^2 during 20 minutes.

3. Results and discussion

The electron-microscopic investigations of the synthesized nanostructures have shown high reproducibility in the precipitation of bismuth at rate of 0.705 μm/min at current density of 20 mA/cm^2 (fig 1,a). At current densities above 25 mA/cm^2 (at voltage above 0.24 V) the hydrogen reduction process begins on the copper sublayer, which prevents the formation of bismuth nanowires in the pores and deposition occurs on the surface of the membrane (fig 1,b). 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. Figure 1,c 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 eV corresponds to aluminium in the PAA structure, with maximum of 0.51 eV – 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 eV, 2.52 eV, 2.57 eV and 2.74 eV) with a maximum band of 2.42 eV.



a) b) c)

Figure 1(a,b,c). (a,b) SEM microphotographs of PAA cross-section with bismuth nanowires, **(c)** spectra of electron probe x-ray spectral microanalysis.

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.

References

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