Thermoelectric Properties of Bi_2Te_3 – Sb_2Te_3 Layers obtained by Pulsed Magnetron Sputtering

Ryszard Mania[a], Elżbieta Godlewska[a], Krzysztof Mars[a], Krzysztof Wojciechowski*[a]
Gabriele Karpinski[b], Paweł Ziolkowski[b], Christian Stiewe[b], Eckhard Müller[b]
a) Faculty of Materials Science and Ceramics
AGH University of Science and Technology,
al. Mickiewicza 30, 30-059 Cracow, Poland
b) Institute of Materials Research, German Aerospace Center (DLR),
Linder Höhe, 51147 Cologne, Germany
e-mail: wojciech@agh.edu.pl

Abstract

Pulsed magnetron sputtering technique was applied for the preparation of the layers of Bi_2Te_3 and Sb_2Te_3. Target materials were synthesized in the evacuated quartz ampoules by melting elemental powders mixed in stoichiometric proportions. The structure and microstructure of targets and prepared films were characterized by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis. Thermoelectric properties were defined by the Seebeck coefficient and electrical conductivity measurements in the temperature range 320 – 430 K. The layers were deposited under various conditions of power (0.09 – 0.20 kW) and current (0.07 – 0.16 A) at the argon pressure of about 3.0 Pa. The efficiency of thermoelectric power obtained for bismuth telluride and antimony telluride were $2 - 4\cdot10^{-4}$ $W\cdot K^{-2}m^{-1}$ and $2 - 6\cdot10^{-3}$ $W\cdot K^{-2}m^{-1}$ respectively. The synthesized materials were used for the fabrication of thermoelectric couples with Bi_2Te_3 as n – type material and Sb_2Te_3 as p – type material. The thermocouples were annealed under vacuum to obtain optimum thermoelectric properties. The Seebeck coefficient of thermocouples was evaluated by Seebeck Scanning Microprobe [1].

Introduction

Thermoelectric materials find application in the construction of electrical power generators or Peltier elements used in thermal stabilization systems. Devices based on thermoelectric materials are characterized by high durability, reliability and maintenance-free operation. Unfortunately, commercial use of thermoelectric elements in such devices as air-conditioners, refrigerators, electrical generators, is limited by their relatively low efficiency, not exceeding 8-12%. Therefore investigations directed at highly efficient thermoelectric materials are gaining in importance.

Thermoelectric materials for practical applications should have high Seebeck coefficient (α), high electrical conductivity (σ) and low thermal conductivity (λ). Those parameters are interrelated by means of thermoelectric figure of merit ZT, which is a measure of the usefulness of thermoelectric materials:

$$ZT = \frac{\alpha^2 \sigma}{\lambda} T \qquad (1)$$

Contemporary thermoelectric devices have figures of merit of about 1 and further improvements can be anticipated through microstructural modifications to take advantage of the quantum effects in nanometric structures [2-3]. Since the characteristic dimensions of thermoelectric structures become progressively smaller [4], there is a great need for special measuring techniques, which would enable measurements in micro- and nanoscale. One of the suitable techniques is that offered by Scanning Seebeck Microprobe, which enables the measurements of the Seebeck coefficient in different points located at a distance of about 10μm.

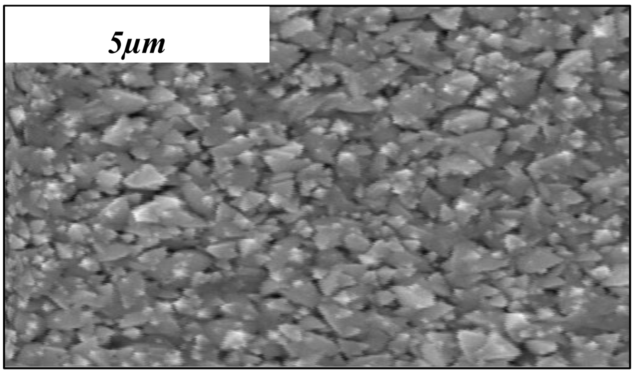
Experimental

The cathode materials, bismuth telluride and antimony telluride, were prepared by melting the components in molar ratios corresponding to the stoichiometry of Sb_2Te_3 and Bi_2Te_3. The reaction products were ground in a mechanical mortar and the resulting powders were hot pressed in graphite moulds, inner diameter of 50mm, to produce cathodes for magnetron sputtering of bismuth telluride and antimony telluride layers. The layers were deposited by means of a single planar magnetron, WMK − 50, driven by a DORA POWER SYSTEM. The best effectiveness, stability and reproducibility of the deposition processes were obtained at current densities of 0.07 – 0.16 A, and power of 0.09 – 0.20 kW. The inert gas pressure in all syntheses was maintained at the level of 3 Pa. Temperature of the substrate was controlled during the deposition process and varied in the range from 310 to 340 K. In order to improve thermoelectric properties, the bismuth telluride and antimony telluride layers were annealed for two hours at 470 K. Junctions of different thermoelectric materials on glass substrates were prepared by using suitable masks.

The layers of thermoelectric materials were next examined in terms of structure and microstructure, electrical conductivity and Seebeck coefficient in the temperature range 310 - 440 K. The properties of thermoelectric layers were studied by means of a Scanning Seebeck Microprobe, which measured local values of the Seebeck coefficient with a resolution of microprobe position about 10μm. As a result, a two-dimensional map was constructed, illustrating the variations of the Seebeck coefficient on the surface of the deposited layers. A characteristic feature of these measurements is that they are made in thermal gradient perpendicular to the layer surface within the region limited to the contact between the sensor tip and the examined specimen. This high resolution of measurements permits precise evaluation of the effect of microstructure, phase composition and anisotropic properties of the material on the value of the Seebeck coefficient.

Results and discussion

Fig. 1 presents the surface (a) and cross-section (b) of a bismuth telluride layer. The layer is polycrystalline, average grain sizes not exceeding 1 µm. Fig. 2 shows the surface (a) and cross-section (b) of antimony telluride. The as-deposited layer was polycrystalline and in spite of appreciable thickness of about 50 µm, it was compact and free of pores or cracks.



a)

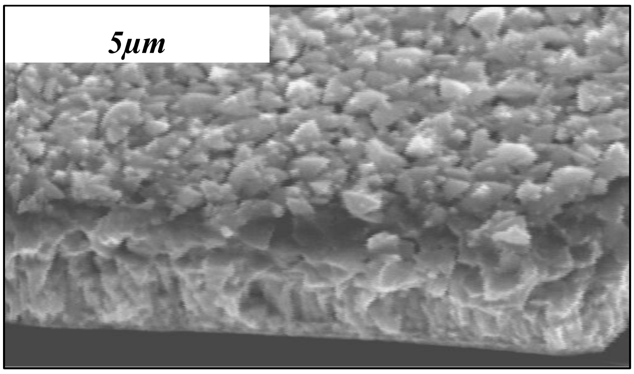


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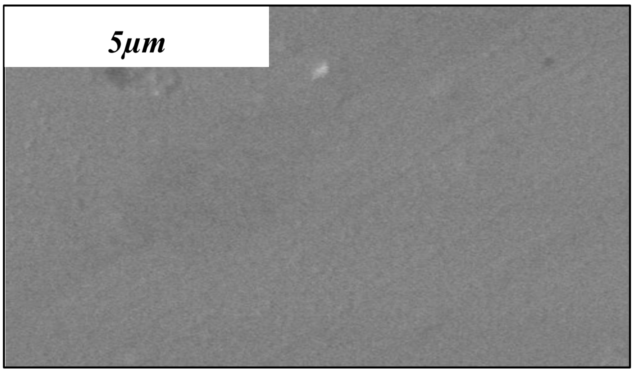
Fig.1. SEM image of the surface (a) and cross-section (b) of the bismuth telluride layer.

The values of electrical conductivity of the heat-treated layers of antimony telluride were significantly higher ($8 \cdot 10^4 \div 1.8 \cdot 10^5$ $S \cdot m^{-1}$) than those of the as-received layers ($1 \cdot 100 \div 4 \cdot 10^3$ $S \cdot m^{-1}$). This behavior was due to the recrystallization and grain growth taking place upon heat treatment. The high electrical conductivity (σ) of material, which at the same time exhibits high value of the Seebeck coefficient (α) favorably influences the power factor ($\alpha^2\sigma$), which for the antimony telluride layers falls in the range 1.25 - $2 \cdot 10\text{-}3 W \cdot K^{-1} m^{-1}$ (Fig.3b). The X-ray diffraction analysis of the Bi_2Te_3 layers confirmed their multiphase composition [5-6]. The values of Seebeck coefficient and of electrical conductivity depend on phase composition of the deposited layer. The examined layer probably contained some amounts of metallic phase BiTe and therefore the measured Seebeck coefficient was close to $-60 \mu V \cdot K^{-1}$. This layer had the highest electrical conductivity of about $8 \cdot 10^4 S \cdot m^{-1}$. The Seebeck coefficient increased with the contribution of Bi_2Te_3 in the layer (about $-130 \mu V \cdot K^{-1}$) and the electrical conductivity attained the lowest value of about $0.5 \cdot 10^4$ $S \cdot m^{-1}$. The values of power factor for the bismuth telluride layers obtained in this work ranged from 0.8 to $4.2 \cdot 10^{-4} W \cdot K^{-1} m^{-1}$ (Fig.3a).



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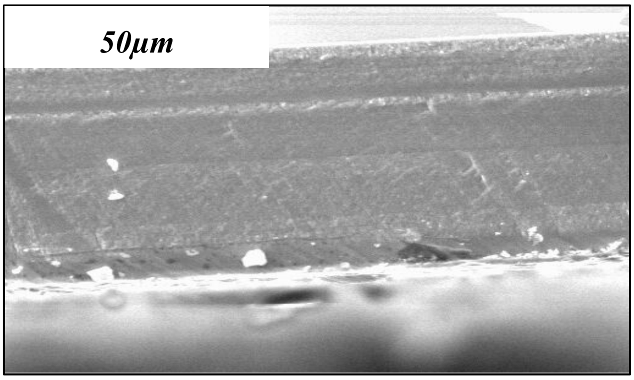
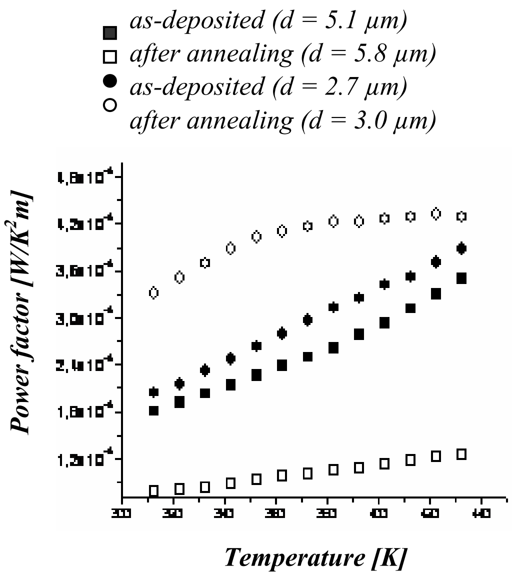


b)

Fig.2. SEM image of the surface (a) and cross-section (b) of the antimony telluride layer.

Figure Fig.4a demonstrates the values of the Seebeck coefficient measured in the system composed of two different thermoelectric materials and two electrical contacts. The results indicate four zones, characterized by different values of the Seebeck coefficient. These zones are clearly separated one from another with well-defined edges, and represent two thermoelectric materials, junction thereof and two electrical contacts. Figure Fig.4b illustrates distribution of standard deviation of the local measurements. For most of the measurements, the standard deviations were small. The only exceptions were lines inclined with respect to the specimen base. In these locations, the standard deviation appeared much higher. This specific pattern reflected temporary disorder of the measuring apparatus. As soon as the problem was settled, the results of measurements were consistent. Fig.4c presents a histogram of the results indicating clearly a multimodal distribution of the measured property; the four maxima corresponding to four zones characterized by different values of the Seebeck coefficient.



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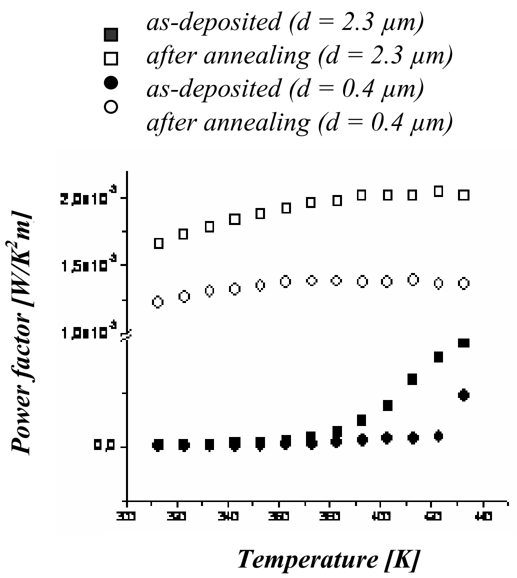
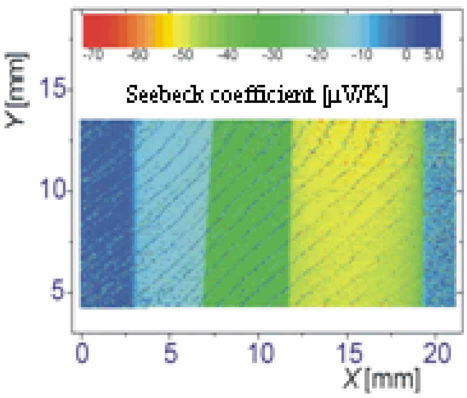


b)

Fig.3 Temperature dependence of the power factor for the layers of bismuth telluride (a) and antimony telluride (b)



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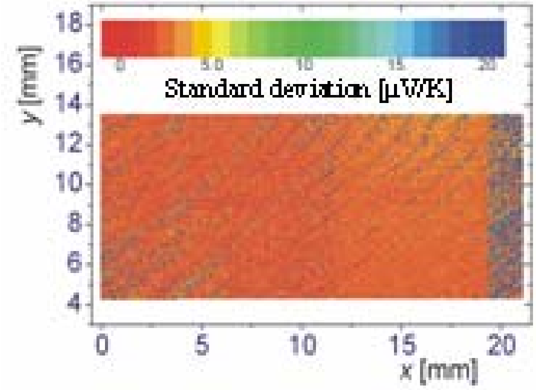

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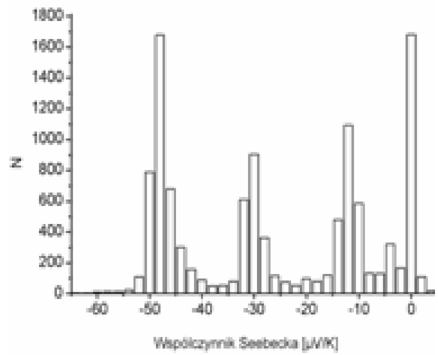

c)

Fig..4 Values of the Seebeck coefficient over a junction composed of two thermoelectric materials and two electrical contacts (a), standard deviations of the measured values (b), histogram (c).

4. Conclusions

The investigations carried out in this work, comprising synthesis of thermoelectric materials and measurements of their thermoelectric properties indicated usefulness of the pulsed magnetron sputtering technique in the manufacturing of bismuth telluride and antimony telluride layers on selected substrates. The Scanning Seebeck Microprobe appeared a very efficient tool for characterizing thermoelectric properties of materials in the form of complex layered structures.

Acknowledgments

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