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Thermoelectric properties of bismuth telluride synthesized by electrochemical deposition method

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Abstract. The paper presents the study of thermoelectric properties of bismuth tellurides obtained by the method of electrochemical deposition. Measurements of electrical conductivity and the Seebeck coefficient were carried out on a NETZCH SBA 458 Nemesis® measuring installation. Based on the obtained measurements, the following conclusions were made: for samples synthesized by the method of continuous electrochemical deposition, the maximum value of the Seebeck coefficient reached α = 14 μV / K, while for samples obtained by the pulse method α = 47 μV / K. It was also noted that after annealing, the samples showed an increase in the Seebeck coefficient up to 1.5 times. As a result of analyzing the measured thermoelectric characteristics, it was concluded that the method of pulsed electrochemical deposition is more efficient for obtaining high-quality thermoelectric materials.

1. Introduction
The modern world is hard to imagine without the elements and devices of microelectronics. And they all need sources of electrical energy [1-8]. Today, one of the types of such sources are microthermoelectric generators (TEG) based on bismuth tellurides (Bi_2Te_3) synthesized by electrochemical deposition [9-11]. Films made from this compound have a high Seebeck coefficient and low values of electrical resistivity. In turn, the data on the physical parameters of thermoelectric materials are used in modeling promising types of thermoelectric generators [12-16]. The purpose of this work is to study the thermoelectric properties of bismuth tellurides obtained by the method of electrochemical deposition.

2. Synthesis of samples
The electrochemical reaction was carried out in a three-electrode cell by the pulse method based on [17]. A silicon substrate with a seed layer of Cr-Cu-Ti is used as a working electrode. A platinum mesh is used as a counter electrode. In the role of the reference electrode is a silver chloride electrode. The three-electrode cell circuit is shown in figure 1.

During the synthesis time, current density, pulse time and frequency were monitored. The type of samples obtained is illustrated in figure 2. Three series of samples of 2 each were synthesized. One of them was subjected to additional annealing. The synthesis parameters of the series of samples are given in Tables 2-4.

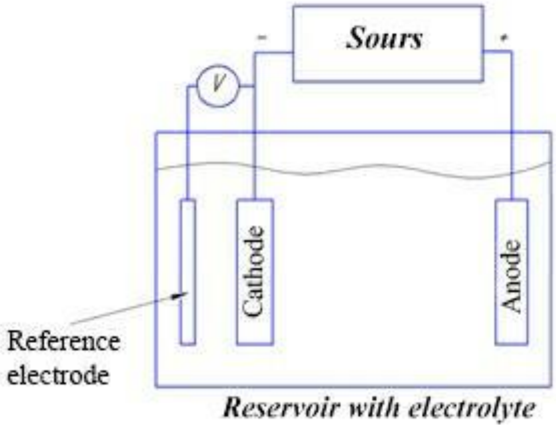

Figure 1. Treelectrode cell diagram.

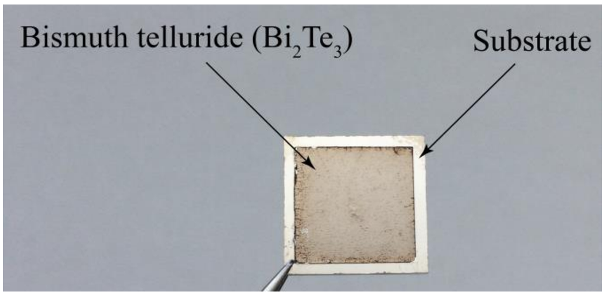

Figure 2. A sample of a thick bismuth telluride film Bi2Te3.

3. Measurement of thermoelectric properties of samples

The efficiency of thermoelectric materials is determined by a dimensionless quantity called thermoelectric figure of merit:

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

where σ is the conductivity of the material, λ is the thermal conductivity, α is the Seebeck coefficient (thermos emf), T is the temperature.

Today, a material having ZT = 1 at room temperature is considered effective. From the formula (1) it is seen that the quality factor will be the higher, the higher the thermos emf and the electrical conductivity of the material. These parameters are directly dependent on the electronic characteristics of the material, and for convenience, they introduce a power factor:

$$P = \sigma \alpha^2 .$$

The thermoelectric parameters of bismuth telluride were measured using the NETZCH SBA 458 Nemesis® measuring system. This setup allows you to measure the Seebeck coefficient and electrical conductivity depending on temperature. The diagram of the measuring cell is shown in figure 3.

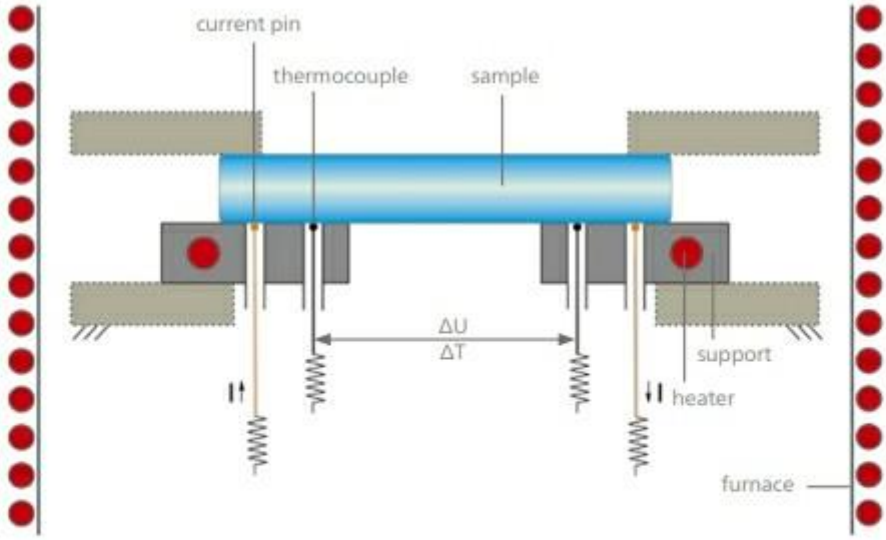

Figure 3. NETZCH SBA 458 Nemesis® measuring cell diagram.

The sample is placed on the ceramic supports, inside of which microheaters are located. Two thermocouples and two current probes are connected to the bottom surface of the sample. Electrical conductivity is measured by the four-point method. This scheme allows current to flow through the sample in the forward and reverse directions. During the measurement, three current values are passed in each direction – I_{max}, $^{2}/_{3}\,I_{max}$, $^{1}/_{3}\,I_{max}$. The value of I_{max} is selected based on the geometry and material of the sample. The program determines three current values, and applies each sample to the sample five times in the forward direction and five times in the opposite direction. Next, the voltage values U_A and U_B are measured between two positive and two negative thermocouple branches. On the basis of the measurements, a graph of voltage dependence on the missed current is plotted, and the electrical conductivity is calculated.

To measure the Seebeck coefficient using two microheaters inside the sample, a temperature gradient is created. After heating one side of the sample, it cools. Then, the other side of the sample is also heated and cooled. During this whole process, the values of the voltages U_A, U_B and U_{T1}, U_{T2} are measured. As for electrical conductivity, U_A and U_B are the voltages between the positive and negative branches of thermocouples. These values are measured with respect to the temperature difference ΔT, which is the temperature gradient between the two sides of the sample. The value of ΔT is determined from the voltages U_{T1} and U_{T2}, coming from two thermocouples. Based on the measurement data, a graph of voltage versus temperature is plotted and the Seebeck coefficient is calculated. In this case, it is ± 2 degrees from the point given by the operator.

4. Results

The measurements were carried out in the temperature range from 20 to 150 ºC. The measurement results are presented in figures 3-5.

Table 1. The synthesis parameters of the samples of series 1.

Sample	Deposition time, h	Deposition current density, mA/sm^2	Thickness, μm	Annealing time, min	Annealing temperature, ºC
1.1	21	3,3	30	–	–
1.2	21	3,3	30	60	240

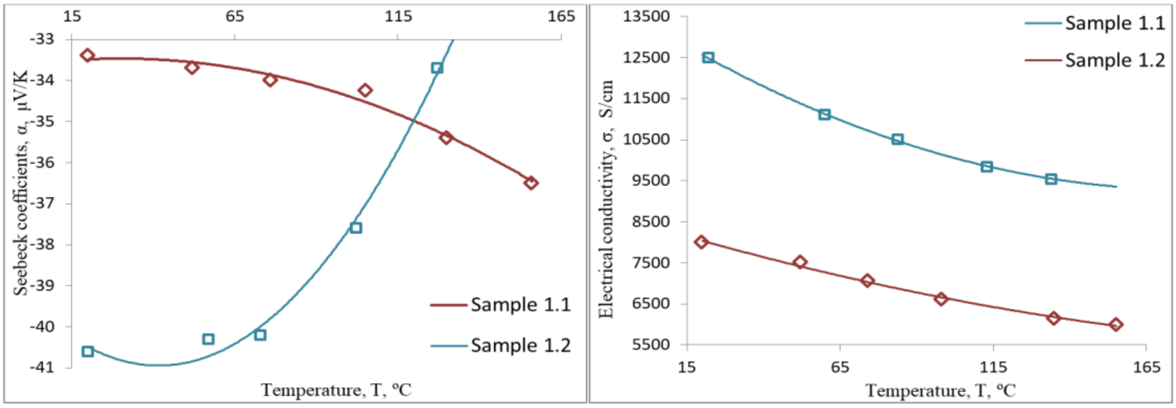

Figure 4. Temperature dependences of the Seebeck coefficient and electrical conductivity for samples of series 1 (red lines - samples without annealing, blue lines - samples with annealing).

Table 2. The synthesis parameters of the samples of series 2.

Sample	Deposition time, h	Deposition current density, mA/sm^2	Thickness, µm	Annealing time, min	Annealing temperature, °C
2.1	7,5	3,3	10	–	–
2.2	7,5	3,3	10	120	230

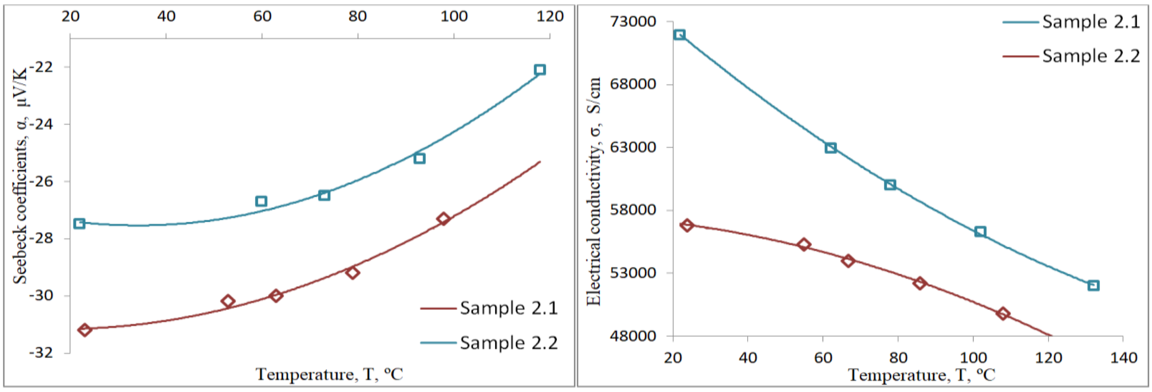

Figure 5. Temperature dependences of the Seebeck coefficient and electrical conductivity for samples of series 2 (red lines - samples without annealing, blue lines - samples with annealing).

Table 3. The synthesis parameters of the samples of series 3.

Sample	Deposition time, h	Deposition current density, mA/sm^2	Thickness, µm	Annealing time, min	Annealing temperature, °C
3.1	11	1,97	25	–	–
3.2	11	1,97	25	60	240

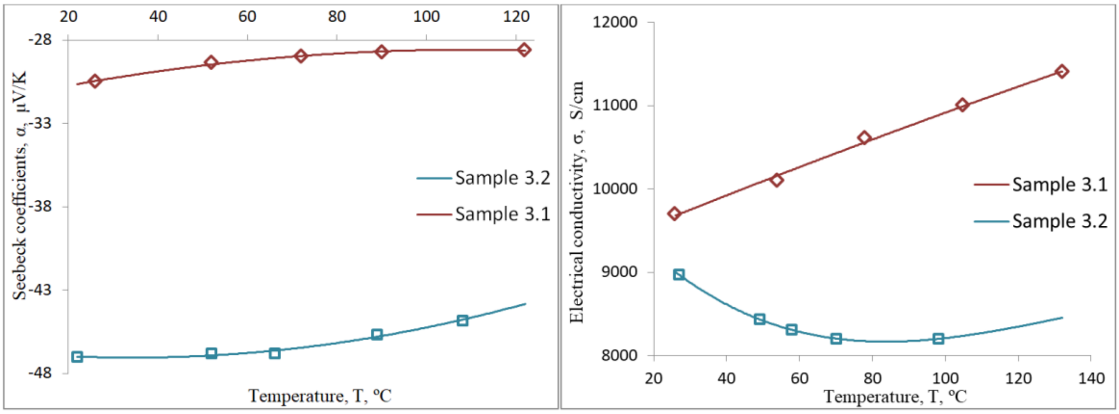

Figure 6. Temperature dependences of the Seebeck coefficient and electrical conductivity for samples of series 3 (red lines - samples without annealing, blue lines - samples with annealing).

5. Conclusion

The resulting solid solutions of bismuth telluride (Bi_2Te_3) are *n*-type semiconductors. The highest value of thermo emf at sample 3.2. Annealing was applied to this sample, which increased the Seebeck coefficient by more than 1.5 times, relative to sample 3.1. Also, for this pair of samples, the value of current density was 1.97 mA / cm^2, whereas for other samples obtained by the pulse method, it was equal to 3.3 mA / cm^2. And since the structure of the material largely depends on the deposition current density, it can be assumed that such a jump in thermo emf after annealing is also related to the deposition conditions. Since at lower values of current density, precipitation occurs more evenly.

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