XIV International Mineral Processing and Recycling Conference
Belgrade, Serbia, 12-14 May 2021

THERMOELECTIC MATERIALS APPLICATION AND THEIR CONTRIBUTION TO PROVIDING CLEANER ENERGY

Emina Požega[1#], Danijela Simonović[1], Saša Marjanović[2], Milenko Jovanović[1], Zdenka Stanojević Šimšić[1], Slađana Krstić[1], Miomir Mikić[1]
[1] Mining and Metallurgy Institute Bor, Bor, Serbia
[2] University of Belgrade, Technical Faculty in Bor, Bor, Serbia

ABSTRACT – The $Bi_2Te_{2.88}Se_{0.12}$ single crystal was grown using the Czochralski technique. Hall and Van der Pauw method were used for the monocrystal characterization. Mobility and concentration of charge bearers majority and Hall coefficient of single crystal were determined. For the sample of BiTe doped with selenium Hall effect was measured at room temperature with an applied magnetic field strength of 0.37 T at different current intensities. The Hall coefficient value is negative, which shows that the samples are n type and that the charge carriers majority are electrons. The fact that the samples are n type was also confirmed by the hot point method.

Keywords: Czochralski Technique, Hall and Van der Pauw Method, Doping.

INTRODUCTION

Thermoelectric materials have unique dual capability of directly converting heat into electricity or electrical power into cooling or heating. They receiving increasing attention due to their potential to make important contributions to the effort on reducing CO_2 and greenhouse gas emission and providing cleaner forms of energy [1,2]. The best known commercially used thermoelectric material (TE) in the bulk form for cooling and power generation applications at ambient temperature is bismuth telluride (Bi_2Te_3), including p-type $Bi_xSb_{2-x}Te_3$ and n-type Bi_2Te_3-ySey [3]. The Bi_2Te_3 based single crystal bulks have the lamellar structure and the weak Van der Waals bonding between Te(1)-Te(1), which is responsible for the easy cleavage along the planes perpendicular to the c-axis. Because this unique structural anisotropy, thermoelectric properties of n-type Bi_2Te_3-*y*Se*y* single crystal solid solutions prepared by traveling heater method shows strong anisotropy. The electrical and thermal conductivities along the cleavage planes (perpendicular to the *c*-axis) are about four and two times larger than those along the *c*-axis, respectively.

Hall effect measurements are important to semiconductor material characterization. From the Hall voltage, the conductivity type, carrier density, and mobility can be derived. With an applied magnetic field, the Hall voltage can be measured.

The Van der Pauw method was first propounded by Leo J. van der Pauw in 1958 [4,5]. This technique commonly used to measure the Hall coefficient of a sample and the resistivity. This method employs a four-point probe placed around the perimeter of the sample. This allows the van der Pauw method to provide an average resistivity of the

corresponding author: emina.pozega@irmbor.co.rs

sample. From the measurements made, the resistivity of the material, the doping type, the number of majority carriers per unit area and the mobility of the material majority carrier can be calculated. The measurements require that four ohmic contacts be placed on the sample. Sample thickness must be much less than the width and length. Symmetrical of the sample reduce errors in the calculations.

In this paper we report results for $Bi_2Te_{2.88}Se_{0.12}$ single crystal obtained by Hall and Van der Pauw method.

EXPERIMENTAL METHOD

Hall-based measurements were performed on an Ecopia device, HMS-3000. The Hall Effect Measurement System HMS-3000, manufactured by Ecopia, is designed to measure the concentration of charge carriers, mobility, specific resistance and Hall coefficient, with the aim of enabling easier and simpler observation of the semiconductor samples electrical characteristics.

Ecopia HMS-3000 set (Figure 1) consists of an adjustable constant current source, software part system, low temperature measurement system and a source of magnetic flux density in the form of a permanent magnet (magnetic set). The system for measuring at different temperatures and the source of magnetic flux density in the form of a permanent magnet (Figure 1 b) physically represent one whole, which has, in addition to the stated roles, also the task of the input part of the whole system (main role).

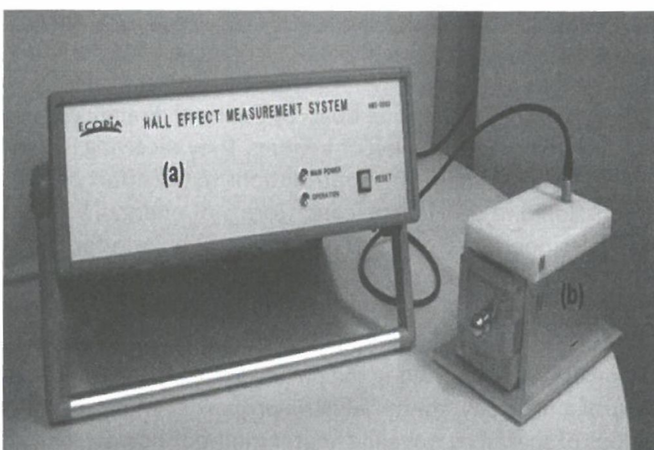

Figure 1 Ecopia HMS-3000 set

An important property of this measurement system is that different data can be calculated and displayed automatically at once (graphically and tabular), after the measurement has been performed on a material single sample. The data obtained after the measurement are: surface carrier concentration, mobility, specific resistance, conductivity, Hall coefficient, magnetic resistance (occurrence of resistance change when the sample is exposed to a magnetic field), alpha (horizontal / vertical resistance ratio), etc., as well as a graphical representation of voltage dependence and current resistance (U-I, R-I graphs).

RESULTS AND DISCUSSION

The samples tested by the Hall and Van der Pauw method were cut from different parts of the ingot normally to the crystallization direction (⊥). In the following, these samples will be referred to as 1/5 (⊥) and 2/2 (⊥), respectively.

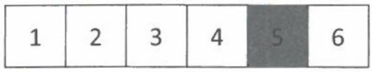

Figure 2 Schematic representation of the location from which the 1/5 (⊥) sample was cut from the ingot

The sample 1/5 (⊥) of circular cross-section is 2.05 mm thick. On Figure 2 the crystal growth beginning is the location one.

Before the measurement starting, it is necessary to prepare the samples and connect them to the PCB holders. The samples on which the measurements were performed had a uniform thickness and did not have any irregularities on them. They prepared to be in the form of thin disc (Figure 4) cut perpendicular to the long axis of a single crystal ingot. All samples were carefully inspected for cavities and scratches and polished if necessary. All measurements were carried out at room temperature (T=300 K). The source of magnetic field applied perpendicular to the Hall element was a permanent magnet of 0.37 T. Hall effect measurements were done to obtain transport properties.

For resistance measure, voltage and current contacts were attached to 4 fixed contact terminals located at the sample ends and at different current intensities. Schottky contacts were used for tests performed at room temperature. The change of transport and electrical parameters with increasing current intensity was also monitored.

Table 1 The results of the Hall and Van der Pauw method for the sample 1/5 (⊥)

Current intesity I [mA]	Bulk carrier concentration n_b [/cm^3]	Sheet carrier concentration n_s [/cm^2]	Mobility μ [cm^2/Vs]	Average Hall coefficient R_H [cm^3/C]
0.1	-1.010×10^{18}	-2.070×10^{17}	6.698×10^{2}	-6.180×10^{0}
0.5	8.546×10^{18}	1.752×10^{18}	2.892×10^{2}	7.304×10^{-1}
1	-7.684×10^{18}	-1.576×10^{18}	2.517×10^{2}	-8.124×10^{-1}
5	-2.268×10^{19}	-4.650×10^{18}	1.356×10^{2}	-2.752×10^{-1}

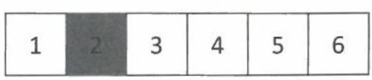

Figure 3 Schematic representation of the location from which the 2/2 (⊥) sample was cut from the ingot

The sample 2/2 (⊥) of circular cross-section is 1.9 mm thick.

Table 2 The results of the Hall and Van der Pauw method for the sample 2/2 (⊥)

Current intesity I [mA]	Bulk carrier concentration n_b [/cm^3]	Sheet carrier concentration n_S [/cm^2]	Mobility μ [cm^2/Vs]	Average Hall coefficient R_H [cm^3/C]
0.1	7.828×10^{17}	1.487×10^{17}	1.082×10^{3}	7.974×10^{0}
0.5	-2.525×10^{18}	-4.797×10^{17}	6.982×10^{2}	-2.472×10^{0}
1	-3.659×10^{19}	-6.951×10^{18}	5.810×10^{1}	-1.706×10^{-1}
5	-1.050×10^{19}	-1.996×10^{18}	2.238×10^{2}	-5.943×10^{-1}

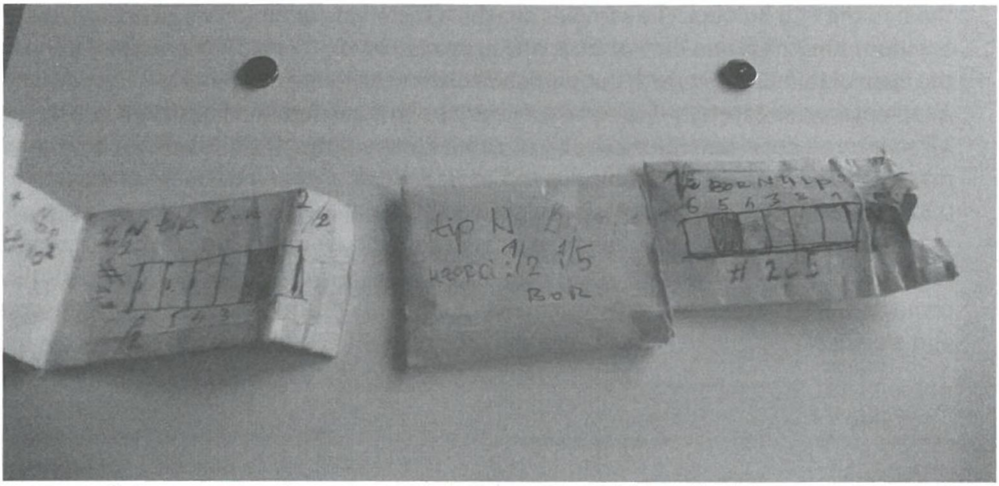

Figure 4 Cross-sectional view of a circular samples 1/5 (⊥) and 2/2 (⊥), cut from the ingot

The calculated data from the measurement results of the transport quantities for samples 1/5 (⊥) and 2/2 (⊥) with a Schottky diode at room temperature (25 °C) and magnetic induction of the permanent magnet B = 0.370 T are given in Tables 1 and 2. Measurements were performed at currents of: 0.1; 0.5; 1; and 5 mA. The concentration of the carrier charge increases with increasing current for both samples and ranges from 1017 to 1019 cm^{-3}. The power factor is related to the concentration of the carrier charge and is maximized by nb~1020 cm^{-3} in semiconductors [6,7]. The Hall coefficient values are negative except for the sample 1/5 (⊥) at a current of 0.5 mA and for the sample 2/2 (⊥) at a current of 0.1 mA. This indicates that the samples are of n type and that the charge carriers majority are electrons. That the samples are of n type was also confirmed by the hot point method. The mobility of most charge carriers decreases with increasing current, which indicates that the temperature of the samples increases, which affects on the mobility. For the sample 1/5 (⊥) the value of μ is less than the value of n type bismuth telluride mobility which is 510 cm^{2}V^{-1}s^{-1} [8].

CONCLUSION

This paper was the result of the properties testing of an selenium doped bismuth telluride semiconductor monocrystalline compound. Hall's and Van der Pauw's methods were used for material characterization.

An selenium doped bismuth telluride monocrystal was synthesized. The electrical properties of this crystal were measured and the mobility, concentration of the charge carriers majority and Hall coefficient were observed. On the basis of the Hall coefficient, it was determined that in the monocrystal the majority carriers are electrons. The measured electrons mobility was significantly less than the electron mobility in pure bismuth telluride.

The results of these studies show that the selenium doped bismuth and tellurium monocrystal was successfully synthesized by the Czochralski method, and significantly complement existing bismuth telluride single crystals knowledge.

ACKNOWLEDGEMENT

Authors wish to thank Professor Academician Pantelija Nikolić on big and selfless efforts and assistance in all stages of investigations. As well authors wish to thank Stevan Vujatović, a specialized technician. This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Grant No. 451-03-9/2021-14/ 200052.

REFERENCES

1. Yan, X., Poudel, B., Ma, Y., Liu, W.S., Joshi, G., Wang, H., Lan, Y., Wang, D., Chen, G., Ren, Z. F. (2010) Experimental Studies on AnisotropicThermoelectric Properties and Structures of n-Type $Bi_2Te_{2.7}Se_{0.3}$. Nano Letters, 10, 3373–3378.
2. Bell, L.E. (2008) Cooling, heating, generating power and recovering waste heat with thermoelectric systems. Science, 321, 1457-1461.
3. Saleemi, M., Toprak, M.S., Li, S., Johnsson, M., Muhammed, M. (2012) Synthesis, processing, and thermoelectric properties of bulk nanostructured bismuth telluride (Bi_2Te_3). Journal of Materials Chemistry, 22, 725-730.
4. Van der Pauw, L.j. (1958) A method of measuring specific resistivity and Hall effect of discs of arbitrary shape. Philips Research Reports, 13, 1–9.
5. Van der Pauw, L.j. (1958) A method of measuring the resistivity and Hall coefficient on lamellae of arbitrary shape. Philips Technical Review, 20, 220–224.
6. Snyder, G., Toberer, E. (2008) Complex thermoelectric materials. Nature materials 7, 105-114.
7. Požega, E. (2018) Sinteza i karakterizacija monokristala bizmuta i telura dopiranih selenom, cirkonijumom i arsenom (Doktorska disretacija). Univerzitet u Beogradu, Tehnički fakultet u Boru, Bor.
8. Gol'cman, B.M., Kudinov, V.A., Smirnov, I.A. (1972) Semiconductor thermoelectric materials based on Bi_2Te_3. 2nd ed. Moskva: Nauka (in Russian).