International Journal of Pure and Applied Physics
ISSN 0973-1776 Volume 4 Number 1 (2008) pp. 1–12
© Research India Publications
http://www.ripublication.com/ijpap.htm

Density of States Effective Mass of $SnBi_4Se_7$ Deduced From the Temperature Dependence of Electrical Conductivity in the Activation Regime

S.A. Ahmed*, A.K. Diab and A.M. Abdel Hakeem

Physics Department, Faculty of Science,
Sohag University, 82524 Sohag, Egypt
E-mail: Saadzf2003@yahoo.com. (S. A. Ahmed)
**Corresponding author: Girls College of Education,*
P.O. Box 3137, Unaizah 51911, Qassim - Kingdom of Saudi Arabia

Abstract

Current-voltage (I-V) measurements on polycrystalline samples of Bi_2Se_3 and stoichiometric ternary compound in the quasi-binary system SnSe-Bi_2Se_3 at different temperatures in the vicinity of room temperature have been performed. Also, temperature dependence of electrical conductivity has been measured. From the analysis of the temperature dependence of electron concentration in the activation regime above room temperature, the density of states effective mass m* has been determined. Some intrinsic and contact properties such as barrier heights, ideality factors and carriers concentrations have been investigated using I-V characteristics. It has been found that all samples exhibit ohmic and space charge limited conduction at low and high fields, respectively.

PACS: 71.18.+y, 71.20.-b, 71.55.-i, 72.15.-v, 72.20.-i

Keywords: Semiconductors; Electrical conductivity; I-V characteristics; Density of states effective mass

Introduction

Bi_2Se_3 and their solid solutions are nowadays applied in the construction of thermoelectric generators and coolers, operating in the temperature range around 300 K [1]. Therefore, studies of the effect of impurities on the physical properties of Bi_2Se_3 are interesting for basic and applied research.

In more recent years considerable attention has been focused on Bi_2Se_3 and their solid solutions. Structural, electrical and optical properties are reported by a few investigators [2-9]. Navratil et al. [10] reported that the calculated value of density of state effective mass for Bi_2Se_3 is $m^* = 0.15m_e$. On the other hand, according to Nikam et al. [11], films of Bi_xSe_{1-x}, where x is greater than 0.6, exhibit ohmic conduction and those with x varying between 0 and 0.6 show nonohmic conduction.

From the survey of literature it can be seen that almost no attempt has been made to determine the density of states effective mass m^* from the electrical properties and the I-V characteristics in the vicinity of room temperature of the mixed crystals in the SnSe- Bi_2Se_3 (Corresponding to the stoichiometry $SnBi_4Se_7$) system. Hence, this art have been suggested for studying in the present work. Therefore, it was thought that it would be very interesting to investigate electrical transport properties of this system over the entire range of temperature.

Experimental Procedure

The binary tin and bismuth selenides (SnSe and Bi_2Se_3) were prepared by a solid-state reaction from 5N purity elements, while the ternary compound $SnBi_4Se_7$ was prepared from the binary compounds. The X-ray investigation and other experimental details about the sample preparation are reported elsewhere [2].

The $SnBi_4Se_7$ compound ingot was cut into two parts. One was left as-quenched sample and the other was annealed, which was heated in an evacuated furnace at 573 K for 60 minutes. This temperature was selected to be above the crystallization temperature (553 K), as calculated from the thermal analysis data (DSC).

Bulk samples (the conduction cross-section ~ 0.5 cm^2 and the length ~ 0.3 cm) with parallel and optically flat surfaces were prepared by a wire saw with a 600- mesh silicon carbide slurry. The best crack-free samples were most easily obtained with an acid saw. For cutting samples, a solution of one part HCL, three parts HNO_3 solution was found satisfactory. Polishing was performed mechanically by means of a controlled velocity rotating disc. A technique developed by Sagar and Faust [12] was used to etch the samples in a dilute solution of bromine (10 ml of a stock solution of 10 % bromine in methanol) in methanol (150 ml of methanol), the etching time usually was anywhere from 30 sec to two minutes, then the samples were washed many times in methanol and finally in deionizer water.

The measurements of the current-voltage (I-V) characteristics and d.c electrical conductivity (σ) of as-quenched Bi_2Se_3 and $SnBi_4Se_7$, and annealed $SnBi_4Se_7$ were carried out under vacuum of 10^{-4} mbar, using a pressure contact sample holder. To achieve ohmic contact with the investigated samples a silver paste was used. The achievement of an ohmic contact with the samples is a mandatory condition for investigation of their electrical properties, especially for the $\sigma = f(T)$ dependence. The non-rectifying character of the metal–semiconductor contacts was proved on the basis of the measured current–voltage characteristics. A conventional series electrical current circuit was used. The current was measured directly by means of Gould advance Beta DMM, while the potential difference was measured by means of Keithely 179 microvolt DMM. The sensitivity of measuring current and potential difference was equal to 1 x 10^{-6} A and 1 x 10^{-5} V, respectively. The applied voltage was stepwise swept from zero to the desired value and, in order to reach a steady state, a delay time of 10 up to 30 seconds was used setting the voltage step and the current reading.

For the purpose of determining the barrier heights of contacts, I-V measurements were performed at four temperature values, T = 280, 300, 320 and 340 K, whereas, the dc conductivity measurements were carried out in the temperature range 90-420 K. The temperature was controlled by means of a thermocouple.

Results and discussion

In a better understanding of electrical properties of any semiconductor material, it has great importance to be known for its contact behaviour with several other substances. For this purpose, common analysis methods include current-voltage (I-V), capacitance-voltage (C-V) and photoelectric measurements [13-15].

I-V characteristics obtained at four temperature values for annealed $SnBi_4Se_7$ is shown in Fig. 1 (for example). Similar plots (results not shown) have been obtained for as-quenched Bi_2Se_3 and $SnBi_4Se_7$ under the same conditions. All measurements were performed in a voltage range of ~ -1 V to ~ 1 V. It is found that these curves obey $I \propto V^m$ equation. The value of m is 1 at lower fields (< 1.67 V/cm), suggesting ohmic conduction and is between 1 and 2 at higher fields (> 1.67 V/cm). Since proportion of defects and nonstoichiometry may not be that high in samples studied it does not influence ohmic conduction in low field region. The behaviour at higher fields ($1 \leq m \leq 2$) demonstrates the possibility of space charge limited conduction. Therefore, the I-V characteristics in the forward direction with $V>3k_BT/q$ is given by [16];

$$J = A^{**}T^2 \exp(-q\phi_{B0}/k_BT)\exp(qV/nk_BT) \qquad (1)$$

where A^{**} is the effective Richardson constant, T the absolute temperature, q the electronic charge, φ_{B0} the barrier height at zero bias, k_B the Boltzmann constant and n the ideality factor.

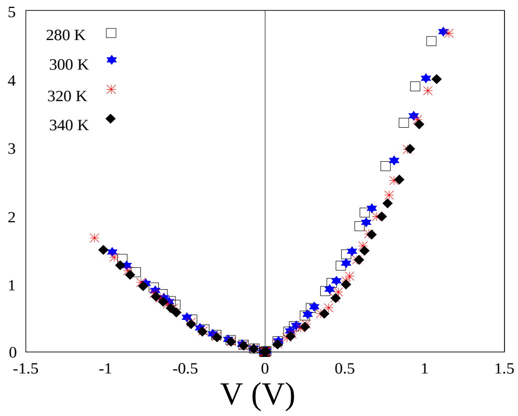

Figure 1 : I-V characteristics for annealed SnBi4Se7 at 573 K for one hour.

For each temperature value, ideality factor, n, was calculated by means of the logarithmic $I-V$ graphs for all samples and given in table 1. These values have been found to be not in any apparent relation with temperature, except for annealed $SnBi_4Se_7$ sample it decreases with increasing temperature. At all considered temperatures, the values of ideality factor for as-quenched $SnBi_4Se_7$ were found to be greater than those for as-quenched Bi_2Se_3, while the values for annealed $SnBi_4Se_7$ were found to be greater than those for as-quenched $SnBi_4Se_7$.

Table 1 : Saturation current densities, ideality factors, carrier concentrations and barrier heights for contacts at different temperatures of as-quenched Bi_2Se_3 and $SnBi_4Se_7$, and annealed $SnBi_4Se_7$ samples.

Sample	Temperature	J_0 (A/m^2)	n	N_D (10^{19}cm^{-3})	φ_{B0} (eV)
as-quenched Bi_2Se_3	280	2.406	1.66	4.2	0.320
	300	2.362	1.57	5.5	0.347
	320	2.321	1.63	8.4	0.374
	340	2.236	1.60	11	0.402
as-quenched $SnBi_4Se_7$	280	2.947	1.87	1.7	0.349
	300	2.835	1.77	2.2	0.379
	320	2.748	1.77	3.6	0.409
	340	2.626	1.63	5.1	0.442
annealed $SnBi_4Se_7$	280	2.664	2.16	2.1	0.335
	300	2.596	2.08	3.4	0.364
	320	2.467	2.00	4.2	0.393
	340	2.378	1.88	6.1	0.423

From the reverse-bias logarithmic $I_R - V$ graphs, saturation current densities were determined for all samples and listed in table 1. The saturation current values were found to be greater for as-quenched $SnBi_4Se_7$ than those for annealed $SnBi_4Se_7$, while the values for annealed $SnBi_4Se_7$ were greater than those for as-quenched Bi_2Se_3. Furthermore, the saturation current densities have been increased with the temperature for all samples. Also, from the variation of $\ln(I_s / T^2)$ with (1000/T), effective Richardson parameters, A^{**}, were determined for as-quenched Bi_2Se_3 and $SnBi_4Se_7$, and annealed $SnBi_4Se_7$ as A^{**}=8.93, 22.65 and 13.53 A/cm^{2}K^2, respectively. By using these values for Richardson constants and also Eq.(1), at four temperature values, the barrier heights were calculated for all samples, and given in table 1. It has been observed an increase for barriers heights with the temperature for all samples.

Furthermore, the apparent built-in potential, V_{bi}, for any contact can be determined by means of the variation of ln(I) with the inverse temperature, 1/T. Therefore, an effective potential, $V_{eff} = V + V_{bi}$ can be introduced and the reverse-bias current density might be written as [16];

$$I_R = I_0 \exp\left[\alpha (V_{eff})^{1/4}\right] \tag{2}$$

Here, α is defined as follows:

$$\alpha = \frac{q}{k_B T}\left(\frac{q}{4\pi\varepsilon_s}\right)^{1/2}\left(\frac{2qN_D}{\varepsilon_s}\right)^{1/4} \tag{3}$$

where ε_s is the dielectric constant of semiconductor material and N_D the donor concentration in n-type semiconductor.

Thus, the α parameter in the above equation, and hence N_D carrier densities can be estimated by plotting the $\ln(I_R) - V_{eff}^{1/4}$ graph for each temperature value. Therefore, for as-quenched Bi$_2$Se$_3$ and SnBi$_4$Se$_7$, and annealed SnBi$_4$Se$_7$ samples, the $\ln(I_R) - V_{eff}^{1/4}$ graphs were plotted in Figs. 2, 3 and 4, respectively. Then, the α parameters found by slopes of curves for each temperature were shown in relevant figures. Taking into account the temperature-independent component of the electrical conductivity, the dielectric constants for all samples are calculated as reported in ref. [17]. The calculated values for the dielectric constants of as-quenched Bi$_2$Se$_3$ and SnBi$_4$Se$_7$, and annealed SnBi$_4$Se$_7$ were 30, 26.4 and 26.69, respectively. Using Eq. (3), the values of N_D concentrations were obtained and listed in table 1 for all samples. The carrier density values were found in agreement with those given in literature survey and comparable with those reported below.

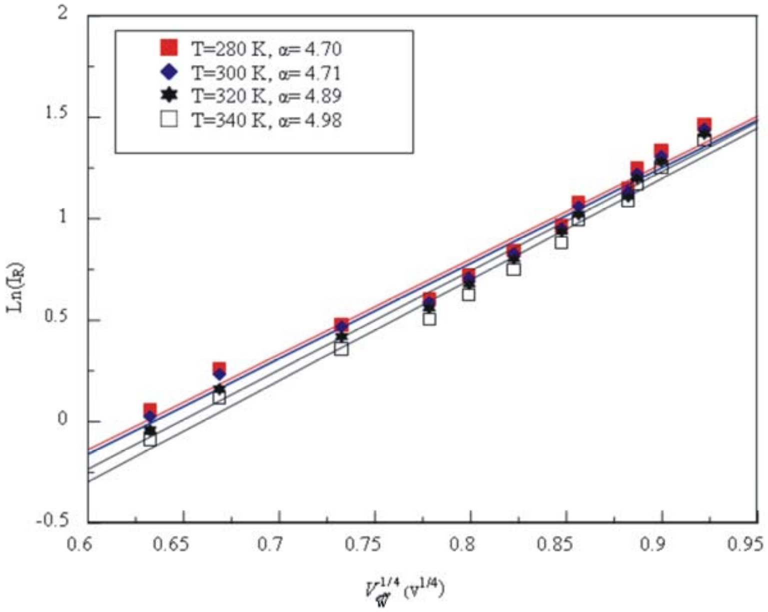

Figure 2 : The variation of reverse current ln(I$_R$) with $V_{eff}^{1/4}$ for as-quenched Bi$_2$Se$_3$. By means of slopes of these curves, α parameter were determined.

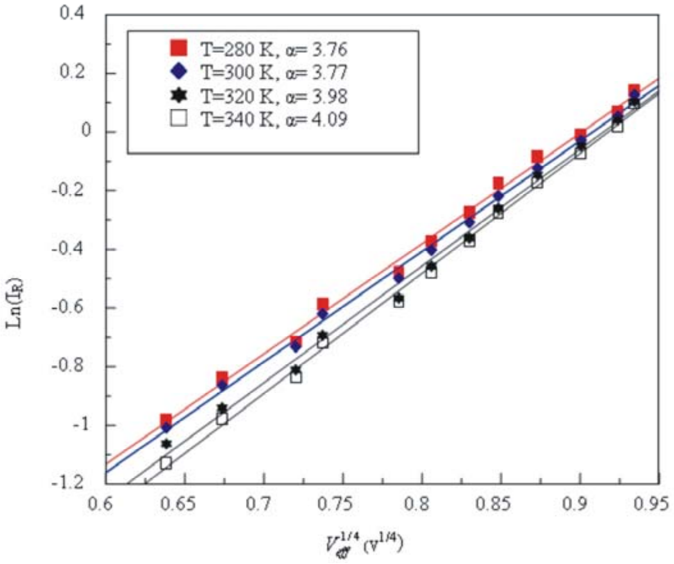

Figure 3 : The variation of reverse current ln(I_R) with $V_{eff}^{1/4}$ for as-quenched $SnBi_4Se_7$. By means of slopes of these curves, α parameter were determined.

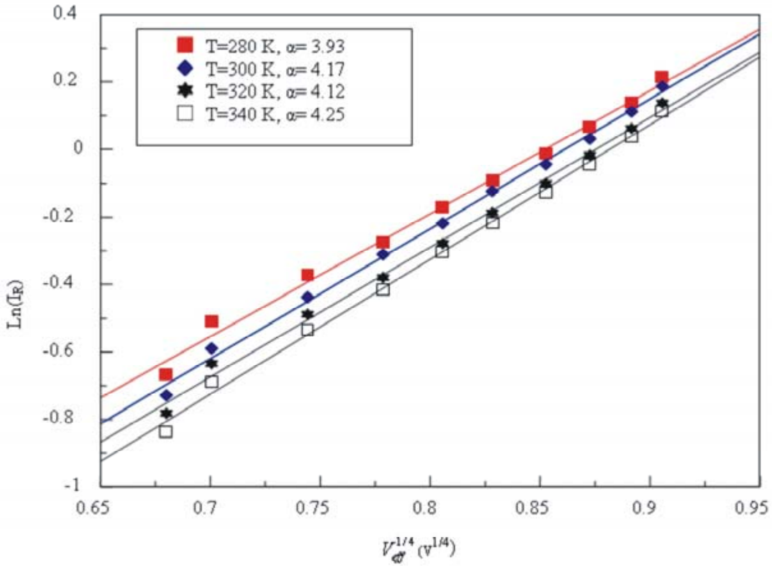

Figure 4 : The variation of reverse current ln(I_R) with $V_{eff}^{1/4}$ for annealed $SnBi_4Se_7$. By means of slopes of these curves, α parameter were determined.

Figure 5 shows the electrical conductivity of as-quenched Bi_2Se_3 and $SnBi_4Se_7$, and annealed $SnBi_4Se_7$ samples as a function of temperature. The electrical conductivity measurements on polycrystalline of as-quenched Bi_2Se_3 showed that the material is a semiconductor with conductivity of ~4.81 $\Omega^{-1}cm^{-1}$ at 420 K which decreases to ~3.66 $\Omega^{-1}cm^{-1}$ at 90 K. While, the electrical conductivity of as-quenched $SnBi_4Se_7$ and annealed $SnBi_4Se_7$ were ~2.51 and 2.92 $\Omega^{-1}cm^{-1}$ at 90 K, respectively.

Hence, showed a metal-like trend decreasing with elevating temperature [3,18-20]. However, it reaches a minimum at 200 [3,18,19] and 290 K [20], respectively and subsequently increases. The low values of the electrical conductivity with the weak temperature dependence between 90 and 420 K suggests that these compounds are semi-metal or narrow-bandgap semiconductor and are in a relatively high doping state (degenerate) as prepared. The electrical conductivity value of the annealed SnBi4Se7 sample is high, except at high temperature, compared with that value of the as-quenched sample, as expect. Since annealing has the effect of altering the nature and concentration of defects, as well as promoting grain growth and thus material homogeneity. At high temperature the trend could indicate a correlation between grain size and high temperature performance.

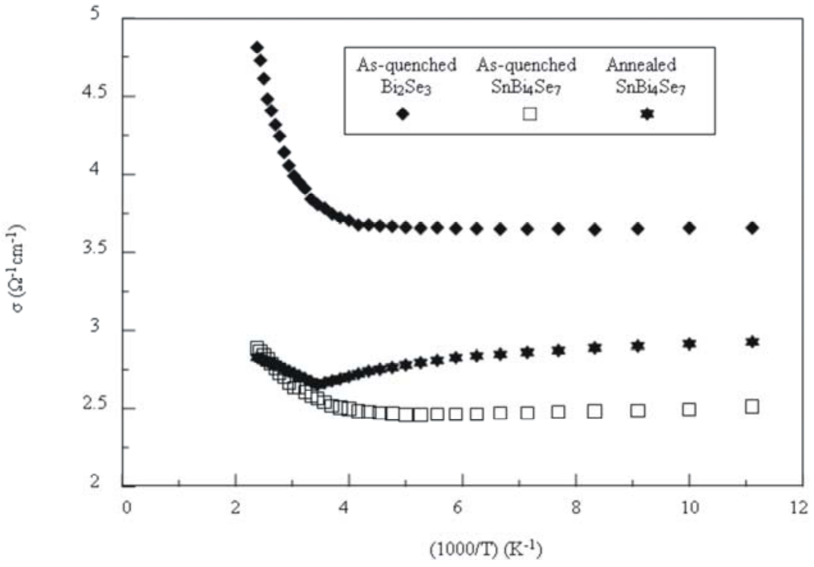

Figure 5 : Electrical conductivity ($\Omega^{-1}cm^{-1}$) versus (1000/T) (K^{-1}) characteristics of as-quenched Bi_2Se_3 and $SnBi_4Se_7$, and annealed $SnBi_4Se_7$ samples.

Accordingly [3,18-20], the metal-like behavior of the charge-transport properties of as-quenched $SnBi_4Se_7$ is, therefore, due to heavy doping occurring during synthesis to the point where these materials can be classified as degenerate semiconductors. Such doping could be brought via slight nonstoichiometry between Sn/Bi, slight Se deficiency or slight Se excess [18]. The negative thermoelectric power of the materials [2] indicates electrons as the carriers and is consistent with slight Se deficiency [18].

In order to gain further information regarding the effect of doping with foreign impurities and annealing process on the shallow donor activation energy, the expression proposed by Blakemore for non-degenerate statistics of the single level, applicable to conduction band electrons which are predominant at higher temperatures, is used [21,22]. This is expressed as [23]:

$$\frac{n_c(n_c + N_A)}{N_D - N_A - n_c} = \frac{N_C}{2}\exp\left[\frac{-E_D}{k_B T}\right] \tag{4}$$

where

$$N_C = \frac{2}{h^3}\left[2\pi m_e^* k_B\right]T^{3/2} \tag{5}$$

In these expressions E_D is the activation energy and m_e^* the effective mass of electrons, n_c the electron concentration in the conduction band, N_D and N_A are the concentration of donors and compensating acceptors, respectively and $k=N_A/N_D$ the compensation ratio. The carrier density n_c was calculated, as that reported in many papers [24-28]. To calculate the values of N_D, N_A and E_D a method, originally proposed by Huston [29] and later successfully employed by Marin et al. [21] and Wasim et al. [22], is used. Following this approach trial values of N_D and N_A are chosen and with the temperature dependence of the calculated n_c, $\ln\left[n_c(n_c + N_A)/(N_D - N_A - n_c)T^{3/2}\right]$ is plotted against 1000/T. If the plot does not give a straight line, new values of N_D and N_A must be chosen and the calculated data are replotted. This process is repeated until a straight line over a temperature range up to 300 K, where the conduction in the activation regime is predominant, is obtained for all samples. This gives the correct value of N_D and N_A. This is shown in Fig. 6, and the values of N_D and N_A are given in Table 2. From the slope of the linear dependence, thus obtained in Fig. 6, E_D is calculated for all samples. Values of E_D estimated from the slope for as-quenched Bi_2Se_3 and $SnBi_4Se_7$, and annealed $SnBi_4Se_7$ samples are also given in Table 2. It can be noticed that the straight lines converge, within an experimental error, to a single point at y-axis (1000/T=0). Since the effective mass m_e^* is calculated from the intercept at y-axis, the convergence confirms that m_e^* does not change for all samples. This type of analysis of the electrical conductivity dependence of temperature, to our knowledge, has not been reported before. This helps us to determine the effective mass, with greater accuracy. The electron effective mass m_e^* of as-quenched Bi_2Se_3 and $SnBi_4Se_7$, and annealed $SnBi_4Se_7$ samples, estimated from the intercept, is given in Table 2. Kuznetsova et al. [20] reported that the calculated density of state effective masses for the ternary Ge(Sn,Pb)Te-Bi_2Te_3 compounds have similar values to those for Bi_2Te_3. Accordingly [30], the density of state effective masses for the ternary compounds of Bi_2Se_3 doped with different foreign elements (Pb-Bi_2Se_3, for example [30]) have similar values to those for Bi_2Se_3. From our study we obtained an average of $m_e^* = 0.15 \pm 0.001$, related to the free electron mass m_0, in excellent agreement with that reported in refs. [10,31].

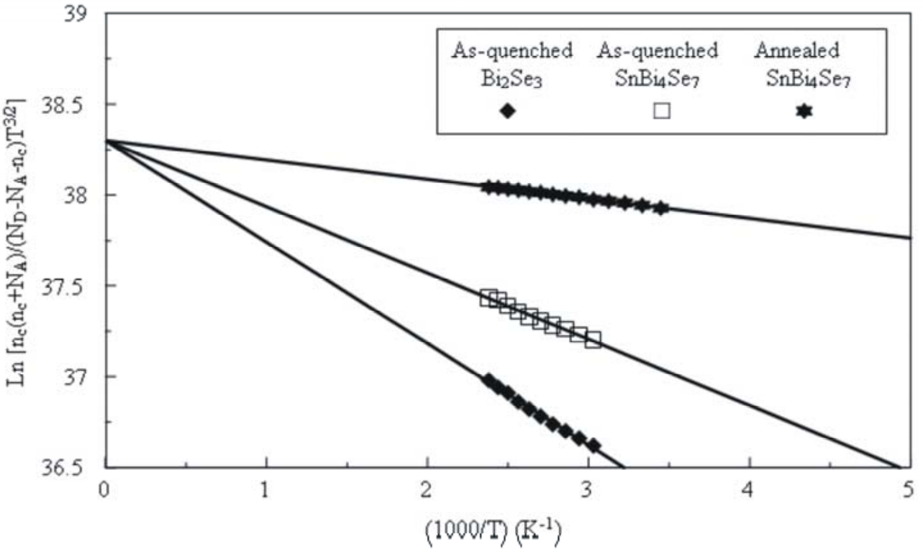

Figure 6 : A plot of $\ln\left[n_c(n_c+N_A)/(N_D-N_A-n_c)T^{3/2}\right]$ against 1000/T for as-quenched Bi_2Se_3 and $SnBi_4Se_7$, and annealed $SnBi_4Se_7$ samples.

Table 2 : Donor and acceptor concentration, compensation ratio, electron effective mass and ionization energies of as-quenched Bi_2Se_3 and $SnBi_4Se_7$, and annealed $SnBi_4Se_7$ samples.

Sample	$N_A\,(10^{19}\text{cm}^{-3})$	$N_D\,(10^{19}\text{cm}^{-3})$	K	$m_e^*.(m_0)$	E_D (meV)
as-quenched Bi_2Se_3	0.71	4.80	0.15	0.149	48.1
as-quenched $SnBi_4Se_7$	0.65	2.73	0.24	0.151	30.9
annealed $SnBi_4Se_7$	0.61	2.52	0.24	0.149	9.2

From the slope of the linear fits in Fig. 6, the activation energy E_D for all samples is calculated. This is given in Table 2. As seen from Table 2, the value of E_D decreases from E_D=48.1 meV to E_D=9.2 meV as the compensation is raised from N_A/N_D=0.15 to N_A/N_D=0.24. Similar behaviour was reported in Ref. [32], and as the ionized impurity is increased as well (to be published elsewhere). Castellan and seitz [33] suggested that the decrease of activation energy with concentration was due to the potential energy of attraction between the ionized donors and conduction electrons. They considered that, this mechanism would lead to lower the activation energy inversely proportional to the average distance between an electron and an ion. Another source of lowering of the activation energy lies in polarization effects. The substitution of Sn atoms for Bi in the Bi_2Se_3 lattice causes an increase in the polarization of the studied samples [34], and lowers the edge of the conduction band

and consequently the activation energy [35]. However, because of the limited number of data points, no conclusive information about E_D in the dilute limit can be obtained from the E_D versus $N_D^{1/3}$ plot [36].

Conclusions

In summary, we have investigated the transport properties of polycrystalline samples of Bi_2Se_3 and stoichiometric ternary compound in the quasi-binary system SnSe-Bi_2Se_3. The current-voltage (I-V) characteristics measurements show Richardson-Schottky emission in high field region. Since proportion of defects and nonstoichiometry may not be that high in samples studied it does not influence ohmic conduction in low field region.

On the other side, the effect of doping with foreign impurities and annealing process in the activation regime above 300 K is studied. The analysis of the temperature dependence of electron concentration, using Blakemore model, permits to estimate the effective mass of the majority charge carrier with greater accuracy for all samples. The value of $m_e^* = (0.15 \pm 0.001) m_0$ has an excellent agreement with those reported earlier.

Acknowledgement

One of the authors (S. A.. Ahmed) would like to thank Professor M. M. Wakkad for critical revising of the manuscript. He is also grateful to Dr. M. R. Ahmed and Dr. S. S. Sheishaa for their helpful english language support.

References

[1] Birkholz, U., 1984, Thermoelektrische Bauelemente, in: "Amorphe und Polykristalline Halbleiter", Heywang, W., ed., Berlin, p. 77.

[2] Ahmed, S. A., 2006, "Preparation and Thermoelectric Power of $SnBi_4Se_7$", Phil. Mag., 86(9), pp. 1227-1241.

[3] Ahmed, S. A., Ibrahim, E. M. M., and Saleh, S. A., 2006, "Electrical Conduction of $SnBi_4Se_7$", Appl. Phys. A, 85, pp. 177-184.

[4] Choi, J., Lee, H.-W., Kim, B.-S., Park, H., Choi, S., Hong, S. C., and Cho, S., 2006, "Magnetic and Transport Properties of Mn-Doped Bi_2Se_3 and Sb_2Se_3", J. Mag. & Mag. Mater., 304, pp. e164-e166.

[5] Urazhdin, S., Bile, D., Mahanti, S. D., Tessmer, S. H., Kyratsi, T., and Kanatzidis, M. G., 2004, "Surface Effects in Layered Semiconductors Bi_2Se_3 and Bi_2Te_3 ", Phys. Rev. B, 69, pp. 85313-85319.

[6] Al Bayaz, A., Giani, A., Foucaran, A., Pascal-Delannoy, F., and Boyer, A., 2003, "Electrical and Thermoelectrical Properties of Bi_2Se_3 Grown by Metal Organic Chemical Vapour Deposition Technique", Thin Solid Films, 441, pp. 1-5.

[7] George, S. D., Augustine, S., Mathai, E., Radhakrishnan, P., Nampoori, V. P. N., and Vallabhan, C. P. G., 2003, "Effect of Te Doping on Thermal Diffusivity of Bi_2Se_3 Crystals: A Study Using Open Cell Photoacoustic Technique", Phys. stat. sol. A, 196(2), pp. 384-389.

[8] Greanya, V. A., Tonjes, W. C., Liu, R., Olson, C. G., Chung, D.-Y., and Kanatzidis, M. G., 2002, "Determination of the Valence Band Dispersions for Bi_2Se_3 Using Angle Resolved Photoemission", J. Appl. Phys., 92(11), pp. 6658-6661.

[9] Urazhdin, S., Bile, D., Tessmer, S. H., Mahanti, S. D., Kyratsi, T., and Kanatzidis, M. G., 2002, "Scanning Tunneling Microscopy of Defect States in the Semiconductor Bi_2Se_3 ", Phys. Rev. B, 66, pp. 161306-161309.

[10] Navratil, J., Plechacek, T., Horak, J., Karamazov, S., Lostak, P., Dyck, J. S., Chen, W., and Uher, C., 2001, "Transport Properties of $Bi_{2-x}In_xSe_3$ Single Crystals ", J. Solid State Chem., 160, pp. 474-481.

[11] Nikam, P. S., and Aher, H. S., 1996, "Conduction Mechanisms in Co-Deposited Bi-Se and Sb-Se Thin Films", Indian J. Pure& Appl. Phys., 34, pp. 393-397.

[12] Sagar, A., and Faust, J. W., 1967, "Dislocation Studies in Bi_2Te_3 by Etch-Pit Technique", J. Appl. Phys., 38, pp. 482-490.

[13] Morsli, M., Amory, C., Bougrine, A., Cattin, L., and Bern`ede, J. C., 2007, "Current–Voltage (*I*–*V*) Studies of Mo/γ-In_2Se_3/ZnO :Al Diode Structures", J. Phys. D: Appl. Phys., 40, pp. 7675-7681.

[14] Mikhelashvili, V., Eisenstein, G., and Uzdin, R., 2001, "Extraction of Schottky Diode Parameters With a Bias Dependent Barrier Height", Solid-State Electron., 45, pp. 143-148.

[15] Sharma, D. K., Narasimhan, K. L., Kumar, S., Arora, B. M., Paul, W., and Turner, W. A., 1989, "Current Transport in *a*-Si:Ge Alloy Schottky Barriers ", J. Appl. Phys., 65(5), pp. 1996-1999.

[16] Sze, S. M., 1981, Physics of Semiconductor Devices, 2nd, John Wiley & Sons, Chapter 5.

[17] Simon, R., 1962, "Thermoelectric Figure of Merit of Two-Band Semiconductors", J. Appl. Phys., 33, pp. 1830-1841.

[18] Chung, D.-Y., Choi, K.-S., Iordanidis, L., Schindler, J. L., Brazis, P. W., Kannewurf, C. R., Chen, B., Hu, S., Uher, C., and Kanatzidis, M. G., 1997, "High Thermopower and Low Thermal Conductivity in Semiconducting Ternary K-Bi-Se Compounds: Synthesis and Properties of β-$K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$ and Their Sb Analogues", Chem. Mater., 9, pp. 3060-3071.

[19] Cho, S., DiVenere, A., Wong, G. K., Ketterson, J. B., and Meyer, J. R., 1999, "Transport Properties of $Bi_{1-x}Sb_x$ Alloy Thin Films Grown on CdTe(111)B", Phys. Rev. B, 59, pp. 10691-10696.

[20] Kuznetsova, L. A., Kuznetsov, V. L., and Rowe, D. M., 2000, "Thermoelectric Properties and Crystal Structure of Ternary Compounds in the Ge(Sn,Pb)Te–Bi_2Te_3 Systems", J. Phys. Chem. Solids, 61, pp. 1269-1274.

[21] Marin, G., Wasim, S. M., Sanchez Perez, G., Bocaranda, P., and Mora, A. E., 1998, "Compositional, Structural, Optical and Electrical Characterization of

$CuInTe_2$ Grown by the Tellurization of Stoichiometric Cu and In in the Liquid Phase", J. Electron. Mater., 27, pp. 1351-1357.

[22] Wasim, S. M., Essaleh, L., Rincon, C., Marin, G., Galibert, J., and Leotin, J., 2005, "Density of States Effective Mass of n-type $CuInSe_2$ From the Temperature Dependence of Hall Coefficient in the Activation Regime", J. Phys. Chem. Solids, 66, pp. 1887-1890.

[23] Blakemore, J.S., 1962, Semiconductors Statistics, Pergamon Press.

[24] Nalos, G. S., Cohn, J. L., Dyck, J. S., Uher, C., and Yang, J., 2002, "Transport Properties of Polycrystalline Type-I Sn Clathrates", Phys. Rev. B, 65, pp. 165201-165206.

[25] Dyck, J. S., Chen, W., Yang, J., Meisner, G. P., and Uher, C., 2002, "Effect of Ni on the Transport and Magnetic Properties of $Co_{1-x}Ni_xSb_3$", Phys. Rev. B, 65, pp. 115204-115212.

[26] Khan, Z. H., Zulfeqaur, M., Kumar, A., and Husain, M., 2002, "Electrical Conductivity and Thermoelectric Power of a-$Se_{80-x}In_x$ and $Se_{80-x}Ge_{20}In_x$ Thin Films", Can. J. Phys., 80, pp. 19-27.

[27] Pujari, V. B., Gaikwad, V. B., Masumdar, E. U., More, P. D., and Deshmukh, L. P., 2002, "Chemically Synthesized (Cd, Hg)Se Pseudobinaries: Some Characteristic Properties", Turk. J. Phys., 26, PP. 407-413.

[28] Osinniy, V., Jedrzejczak, A., Arciszewska, M., Dobrowolski, W., Story, T., and Sadowski, J., 2001, "Fermi Level Position in GaMnAs — A Thermoelectric Study", Acta Phys. Pol. A, 100, pp. 327-334.

[29] Huston, A. R., 1959, "Electronic Properties of ZnO", J. Phys. Chem. Solids, 8, pp. 467-472.

[30] See, for example, Karamazov, S., Horak, J., Navratil, J., and Lostak, P., 1997, "Characterisation of Bi_2Se_3 Crystals Highly Doped With Pb", Cryst. Res. Technol., 32(2), pp. 249-260.

[31] Horak, J., Vlcek, M., Navratil, J., Hu, S., Uher, C., Lostak, P., Drasar, C., and Karamazov, S., 1999, "Characterization of Layered $Bi_{2-x}In_xSe_3$ Single Crystals: The Effect of Indium Incorporation on Thermal Conductivity" Thermal conductivity 25-Thermal Expansion 13, Sci. Pap., Univ. Pardubice, Czech Republic, pp. 106-113.

[32] Essaleh, L., Wasim, S. M., and Galibert, J., 2001, "Effect of Impurity Band Conduction on the Electrical Characteristics of *n*-type $CuInSe_2$", J. Appl. Phys., 90, pp. 3993-3997.

[33] Castellan, G. W., and Seitz, F., 1951, "Semiconducting Materials', Butterworths Scientific Publications, London.

[34] Perez Vicente, C., Tirado, J. L., Adouby, K., Jumas, J. C., Abba Toure, A., and Kra, G., 1999, "X-ray Diffraction and ^{119}Sn Mossbauer Spectroscopy Study of a New Phase in the Bi_2Se_3-SnSe System: $SnBi_4Se_7$", Inorg. Chem., 38, pp. 2131-2135.

[35] Debye, P. P., and Conwell, E. M., 1954, "Electrical Properties of n-type Germanium ", Phys. Rev., 93, pp. 693-706.

[36] Wasim, S. M., and Albornoz, J. G., 1988, "Electrical and Optical Properties of n- and p-type $CuInTe_2$", Phys. Stat. Sol. A, 110(2), pp. 575-583.