Determination of the intrinsic parameters of $SnBi_4Se_7$ via the characterization of electrical properties

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I–V measurements and temperature dependence of electrical conductivity on polycrystalline samples of Bi_2Se_3 and $SnBi_4Se_7$ have been performed. From the analysis of the temperature dependence of electron concentration in the activation regime above room temperature, the effective mass m_e^* has been determined. Some intrinsic and contact properties such as barrier heights, ideality factors, and carrier concentrations have been investigated by using *I–V* characteristics. It has been found that all samples exhibit Ohmic and space charge limited conduction at low and high fields, respectively. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2905262]

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

Considerable attention has been focused on Bi_2Se_3 and their solid solutions,[2–7] since understanding the electronic properties of defects and the ability to control them will be crucial for the performance of the future microelectronic devices. Recently, Ahmed *et al.* reported that doping Bi_2Se_3 with tin atoms results in additional states at the Fermi level[2] and a decrease in the free carrier concentration (electrons), and that the Sn impurity has an acceptor character.[3] Accordingly,[4] the calculated value of m_e^* for Bi_2Se_3 is $m_e^*=0.15m_0$. On the other hand, films of Bi_xSe_{1-x}, where x is greater than 0.6, exhibit an Ohmic conduction and those with x varying between 0 and 0.6 show a non-Ohmic conduction.[5]

Almost no attempt has been made to determine the intrinsic parameters of the mixed crystals in the $SnSe–Bi_2Se_3$ (corresponding to the stoichiometry $SnBi_4Se_7$) system via the characterization of electrical properties. Hence, this art has been suggested for study in the present work.

The binary tin and bismuth selenides, SnSe and Bi_2Se_3, were prepared by a solid-state reaction from 5*N* purity elements, while the ternary $SnBi_4Se_7$ compound was prepared from the binary compounds.

The annealing process for the $SnBi_4Se_7$ sample was achieved in an evacuated furnace at 573 K for 1 h, above the crystallization temperature (553 K), as calculated from the thermal analysis data.

Special attention was paid to fine polishing so that each of the samples (the conduction cross section of ~0.5 cm^2 and the length of ~0.3 cm) has two parallel and optically flat surfaces satisfactory for the proposed measurements.

The measurements of *I–V* characteristics and dc conductivity (σ) of as-quenched Bi_2Se_3 and $SnBi_4Se_7$ and annealed $SnBi_4Se_7$ samples were carried out under a vacuum of 10^{-4} mbar by using a pressure contact sample holder. To achieve Ohmic contact for the $\sigma=f(T)$ dependence with the investigated samples, a silver paste was used. The nonrectifying character of the metal-semiconductor contacts was proved on the basis of the measured *I–V* characteristics. The applied voltage was stepwise swept from zero to the desired value and, in order to reach a steady state, a delay time of 10–30 s was used in setting the voltage step and the current reading. Other experimental details about the contacts and sample preparation are reported elsewhere.[2,3]

I–V measurements were performed at $T=280$, 300, 320, and 340 K, while the dc conductivity measurements were carried out in the temperature range of 90–420 K.

I–V characteristics obtained from annealed $SnBi_4Se_7$ is shown in Fig. 1 (for example). Similar plots (results not shown) have been obtained from as-quenched Bi_2Se_3 and $SnBi_4Se_7$ under the same conditions. It is found that these curves obey the $I\alpha V^m$ 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. Since proportion of defects and nonstoichiometry may not be that high in the samples studied, it does not influence the Ohmic conduction in the low field region. The behavior at higher fields 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[8]

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

where A^{**} is the effective Richardson constant, ϕ_{B0} is the barrier height at zero bias, n is the ideality factor, and J is the current density q and k_B have their useful significance.

For all samples and for each temperature value, the ideality factor (n), saturation current densities (J_0), and the barrier height (ϕ_{B0}) are determined (Table I) as follows. The n factor is calculated by means of ln *I-V* graphs.

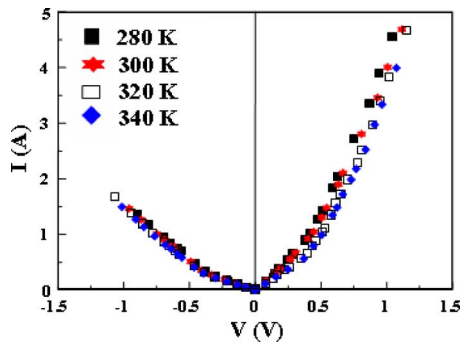

FIG. 1. (Color online) *I–V* characteristics of annealed $SnBi_4Se_7$.

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TABLE I. The intrinsic parameters J_0, n, ϕ_{B0}, α, and N_D for contacts at different temperatures and k, m_e^*, and E_D of all samples.

Sample	k	m_e^* (m_0)	E_D (meV)	T (K)	J_0 (A/m^2)	n	ϕ_{B0} (eV)	α	N_D (10^{19} cm^{-3})
As-quenched Bi_2Se_3	0.15	0.149	48.1	280	2.406	1.66	0.320	4.70	4.2
				300	2.362	1.57	0.347	4.71	5.5
				320	2.321	1.63	0.374	4.89	8.4
				340	2.236	1.60	0.402	4.98	11
As-quenched $SnBi_4Se_7$	0.24	0.151	30.9	280	2.947	1.87	0.349	3.76	1.7
				300	2.835	1.77	0.379	3.77	2.2
				320	2.748	1.77	0.409	3.98	3.6
				340	2.626	1.63	0.442	4.09	5.1
Annealed $SnBi_4Se_7$	0.24	0.149	9.2	280	2.664	2.16	0.335	3.93	2.1
				300	2.596	2.08	0.364	4.17	3.4
				320	2.467	2.00	0.393	4.12	4.2
				340	2.378	1.88	0.423	4.25	6.1

The n values have been found to be not in any apparent relation with temperature except for annealed $SnBi_4Se_7$ where it decreases with increasing temperature. From the reverse-bias $\ln I_R - V$ graphs, the J_0 is determined. It is seen that the J_0 values have been increased with temperature. Also, from the variation of $\ln(I_s/T^2)$ vs $1/T$ (where I_s is the saturation current), the A^{**} parameters are 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. Then, by using Eq. (1), the ϕ_{B0} is calculated. An increase for the ϕ_{B0} values with the temperature has been observed.

Furthermore, the apparent built-in potential (V_{bi}) for any contact can be determined from the variation of $\ln I$ vs $1/T$. Therefore, an effective potential, $V_{eff}=V+V_{bi}$, can be introduced and the reverse-bias current density can be written as[8]

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

Here, α is defined as follows:

$$\alpha = (q/k_BT)(q/4\pi\varepsilon_s)^{1/2}(2qN_D/\varepsilon_s)^{1/4}, \quad (3)$$

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

For estimating the α parameter, and hence N_D carrier densities, the $\ln(I_R)$-$(V_{eff})^{1/4}$ graph for annealed $SnBi_4Se_7$ is plotted in Fig. 2. Similar plots (results not shown) have been obtained for as-quenched Bi_2Se_3 and $SnBi_4Se_7$. Then, the α parameters are found by the slopes of curves (Table I).

By taking into account the temperature-independent component of the electrical conductivity, the dielectric constants for all samples are calculated, as reported in Ref. 9. The calculated values for the dielectric constants of as-quenched Bi_2Se_3 and $SnBi_4Se_7$ and annealed $SnBi_4Se_7$ are 30, 26.4, and 26.69, respectively. By using Eq. (3), the values of N_D concentrations are obtained (Table I). These values are found to be in agreement with those given in literature survey and comparable to those reported below.

The electrical conductivity (σ) as a function of temperature measurements on polycrystalline as-quenched Bi_2Se_3 (see inset in Fig. 3) showed that the material is a semicon-

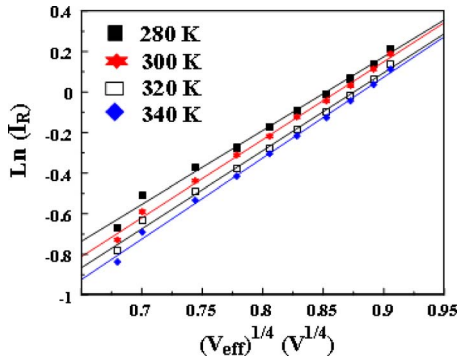

FIG. 2. (Color online) The variation of reverse current $\ln(I_R)$ with $V_{eff}^{1/4}$ of annealed $SnBi_4Se_7$.

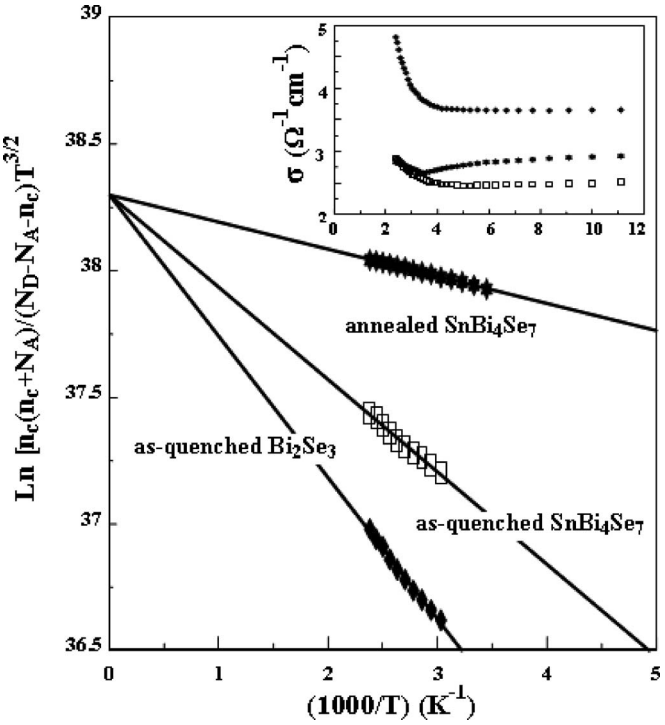

FIG. 3. A plot of $\ln[n_c+N_A)/(N_D-N_A-n_c)T^{3/2}]$ vs $1000/T$ of all samples. The inset shows the electrical conductivity vs $1000/T$.

ductor with σ of $\sim 4.81\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 420 K, which decreases to $\sim 3.66\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 90 K, while σ of as-quenched and annealed $SnBi_4Se_7$ (see inset in Fig. 3) are ~2.51 and $2.92\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 90 K, respectively, and showed a metal-like trend that decreases with elevating temperature.[2,10] However, it reaches a minimum at 200 (Ref. 2) and 290 K,[10] respectively, and subsequently increases. The low values of σ with the weak temperature dependence between 90 and 420 K suggest that these compounds are semimetal or narrow-band-gap semiconductors and are in a relatively high doping state (degenerate) as prepared. It is seen that the σ value of as-quenched Bi_2Se_3 is higher than that of as-quenched $SnBi_4Se_7$ due to decreasing free carrier concentration,[3] as mentioned above. Furthermore, the σ value of annealed $SnBi_4Se_7$ is higher than that of as-quenched $SnBi_4Se_7$ except at a very high temperature, as expected, due to increasing mobility and/or carrier concentration. Since annealing has the effect of altering the nature and concentration of defects, as well as promoting grain growth and thus material homogeneity, at a high temperature, the trend could indicate a correlation between the grain size and high temperature performance.

Accordingly,[2,10] the metal-like behavior of the charge-transport properties of as-quenched $SnBi_4Se_7$ is therefore due to the heavy doping that occurs during synthesis to the point where these materials can be classified as degenerate semiconductors. Such doping could be brought via a slight nonstoichiometry between Sn and Bi, a slight Se deficiency, or a slight excess Se. The negative thermoelectric power of the materials indicates electrons as the carriers and is consistent with a slight Se deficiency.[3]

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[12] for nondegenerate statistics of the single level applicable to conduction band electrons, which are predominant at higher temperatures, is used.[11] This is expressed as[12]

$$n_c(n_c+N_A)/(N_D-N_A-n_c)=(N_c/2)\exp(-E_D/k_BT), \quad (4)$$

where

$$N_c=(2/h^3)(2\pi m_e^* k_B T)^{3/2}, \quad (5)$$

where E_D is the activation energy, m_e^* is the effective mass of electrons, n_c is the electron concentration in the conduction band, N_D and N_A are the concentrations of donors and compensating acceptors, respectively, and $k=N_A/N_D$ is the compensation ratio (Table I). The carrier density n_c is calculated as that reported in many papers.[13] The criteria used[14] to determine the above parameters were to choose values of N_D and N_A until a linear plot of $\ln[n_c(n_c+N_A)/(N_D-N_A-n_c)T^{3/2}]$ vs $1/T$ was obtained (Fig. 3). From the slope of these lines and their intercept on the y axis, E_D and m_e^* are estimated (Table I) and the corresponding values of N_D and N_A are $N_D=4.80,\ 2.73,\ 2.52\times10^{19}\ \mathrm{cm}^{-3}$, and $N_A=0.71,\ 0.65,\ 0.61\times10^{19}\ \mathrm{cm}^{-3}$, for as-quenched Bi_2Se_3 and $SnBi_4Se_7$ and annealed $SnBi_4Se_7$, respectively. It can be noticed that the straight lines converge, within the experimental error, to a single point at the y axis $(1/T=0)$. Since m_e^* is calculated from the intercept at the 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 has not been reported before. This helps us to determine m_e^* with greater accuracy. The calculated m_e^* for the ternary $Pb-Bi_2Se_3$ (Ref. 6) and $Ge(Sn,Pb)Te-Bi_2Te_3$ (Ref. 10) compounds have values similar to those for Bi_2Se_3 and Bi_2Te_3, respectively. From our study, we obtained an average of $m_e^*=0.15\pm0.001$ related to the free electron mass m_0, which is in excellent agreement with that reported in Ref. 4.

As seen from Table I, the value of E_D decreases as the compensation is increased (a similar behavior that was reported in Ref. 15) and as the ionized impurity is increased as well (to be published elsewhere). The decrease of E_D with concentration was due to the potential energy of attraction between the ionized donors and conduction electrons.[16] 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[7] and lowers the edge of the conduction band and, consequently, the activation energy.[17] 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 vs $(N_D)^{1/3}$ plot.[18]

In summary, $I-V$ characteristic measurements show a Richardson–Schottky emission in the high field region.

On the other hand, the analysis of the temperature dependence of electron concentration allows us to estimate m_e^* of the majority charge carrier with greater accuracy for as-quenched Bi_2Se_3 and $SnBi_4Se_7$ and annealed $SnBi_4Se_7$ samples $[m_e^*=(0.15\pm0.001)m_0]$. This value is in excellent agreement with those reported earlier.

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