Transport Properties of Sn and SbI$_3$ Doped Single Crystal p-Bi$_2$Te$_3$

M Z Tahr a, S A Nemov b, D I Popov c and T E Svechnikova d

a Department of Physics, The College at Brockport, State University of New York, Brockport, NY 14420, USA
b State Politechnical University, Politechnicheskaya ul.29, St.-Petersburg 195251 Russia
c ZAO NevInPat, per. Pirogova 7, St.-Petersburg 190000 Russia
d Baikov Institute of Metallurgy and Materials Science, Leninsky pr.49, Moscow 119334 Russia

E-mail: mtahar@brockport.edu

Abstract. Bi$_2$Te$_3$-Sb$_2$Te$_3$ solid solutions, the most commonly used room temperature thermoelectrics, are characterized by inhomogeneities and defects of various types, and doping aggravates the situation with crystal homogeneity. However, several publications reported on unusual behaviour of Sn in Bi$_2$Te$_3$, specifically, on improvement of spatial distribution of Seebeck coefficient over a cleavage face. This work reports on measurements done on single crystals of Bi$_2$Te$_3$ doped with 0.5% Sn as grown by the Czochralski method using a floating crucible. To shift the Fermi level, further doping with the traditional iodine impurity, was introduced as SbI$_3$. X-ray diffraction, $\rho_{\perp}(T)$ (4-point, low freq. A.C.), $\rho_{\perp}(4K, 0 < H < 8T \parallel C_3$-axis), and $R_{Halt}$ measurements were carried out. Two different behaviours are observed: metallic-like resistivity vs. temperature and magnetoresistivity vs. magnetic field for 0.05% SbI$_3$ and non-monotonic resistivity temperature dependence and quantum oscillations in the magnetoresistivity for 0.1% SbI$_3$. The X-ray results and the quantum oscillations indicate the high quality of the single crystals despite the high content of 2 impurities. The observed results are explained by the existence of a band of quasi-local impurity states of Sn located on the background of Bi$_2$Te$_3$ valence band, whose energy levels are estimated.

1. Introduction

Bismuth telluride (Bi$_2$Te$_3$) is the narrow gap semiconductor with $E_g \sim 0.1$ eV. It is of practical importance since it is a foundation compound for developing high efficiency thermoelectric materials used for manufacturing cooling devices operating at room temperatures. Bi$_2$Te$_3$ belongs to the class of layered structures with the structure ($R_{3mm}$). The anisotropy of physical properties and peculiarities in its phase diagram result in the fact that even the most perfect crystals are characterized by a large quantity of various point defects and inhomogeneities ($\sim 10^{19}$ cm$^{-3}$). This leads to considerable fluctuations of the electro-physical properties of crystals and their technical characteristics.

Usually the doping of semiconductors increases the inhomogeneity of samples; however, a number of impurities in narrow gap semiconductors IV-VI ($A^4B^6$) and V-VI ($A^5B^6$) create quasi-local states located on the background of the allowed zone of the conduction electrons. Such an unusual acceptor-like impurity in Bi$_2$Te$_3$ is Sn. According to [1], doping of Bi$_2$Te$_3$ with Sn leads to formation of a band of the quasi-local states on the background of the valence zone (VZ) of Bi$_2$Te$_3$. Also the impurity states of Sn stabilize the concentration of holes in the...
VZ and pin down the Fermi level $E_F$. This results in considerable improvement of a spatial homogeneity of electro-physical properties of crystals $Bi_2Te_3 : Sn$.

The $Bi_2Te_3 : Sn$ crystals studied in the prior work [1] had different content of $Sn$ and location of $E_F$. In order to correctly compare the properties of crystals, it is necessary to fix the content of $Sn$ and to shift the Fermi level by doping with an additional impurity. In view of this, the present work is on samples of $Bi_2Te_3$ doped with 0.5% $Sn$, which were additionally doped with iodine ($I$). The iodine impurity was introduced in the above crystals in the form of $SbI_3$.

2. Experimental Details
The samples were first cleaved and then X-rayed using a Phillips Xpert diffractometer where the sample is fixed and both the X-ray source and detector rotate around the sample with an angular resolution better than a millidegree. The ceramic X-ray tube, which uses copper as a target, is coupled to a state-of-the-art collimator with variable width slit and the detector uses a curved crystal to select the $K_{\alpha 1}$ radiation. The transport measurements were carried out on thin samples ($\sim 80\mu m$), which were cleaved off a thicker slab using adhesive tape, which was subsequently removed using acetone. Four electrical contacts were made using a two component silver loaded epoxy which was cured at 110°C for 10 minutes. Special attention was made for the current contacts across the edge of the sample and the voltage contacts were made in the middle third of the sample to minimize the anisotropy effects and maximize the sensed voltage. Since the materials have thermoelectric properties that may depend on the kind of leads, and the temperature and its gradient through the sample we chose AC excitation current and used a floating current sources [2] and lock-in-detectors at relatively low frequency. Because we measured two samples at a time we chose 7Hz and 13Hz as two prime number frequencies which are neither multiples nor submultiples of the line frequency and cannot interfere with each other constructively. To avoid sample self heating the excitation currents were so that the total power dissipation was under 5\mu W, which is less than the accepted dissipation for the silicon diode used to monitor the temperature of the boron nitride sample holder. The temperature scan were very slow during overnight cooling and warming, to minimize any thermal hysteresis due to sample/thermometer different responses to temperature changes. As for the quantum oscillations, the samples were inserted in a different cryostat with a superconducting magnet capable of generating a 10 Tesla field. This allowed for resistivity reproduceability after thermal cycling to room temperature.

Figure 1. X-ray Diffractogram for $Bi_2Te_3 + 0.5\%Sn + 0.05\%SbI_3$.

Figure 2. X-ray Diffractogram for $Bi_2Te_3 + 0.5\%Sn + 0.1\%SbI_3$. 

3. Results

Here, we present the experimental results, starting with the X-ray diffractograms for the two compositions as shown side by side in Figures 1 and 2, for samples #97 \((\text{Bi}_2\text{Te}_3 + 0.5\%\text{Sn} + 0.05\%\text{SbI}_3)\) and #98 \((\text{Bi}_2\text{Te}_3 + 0.5\%\text{Sn} + 0.1\%\text{SbI}_3)\), respectively. It is clear that the peaks angular positions are identical to within 0.1 of a degree and the peaks’ width variation is less than a few milli-degrees. Further, the peaks’ width at half maximum seem to indicate a coherence length in the direction perpendicular to the basal plane of about 1500\(\AA\) for both samples.

![Figure 3](image3.png)

Figure 3. The resistivity as a function of temperature and as normalized to that at room temperature.

Figure 3 is a graph of the resistivity as a function of temperature in the range of room temperature down to 2K. Actually the graph is that of \(\rho(T)/\rho(300K)\) since the geometrical dimensions of the sample can only be measured at room temperature; the average room temperature resistivities were measured to be 22\(\mu\Omega\)-m and 70\(\mu\Omega\)-m for the two compositions, respectively. As can be seen, one sample (#97) exhibits a metal-like behavior, i.e. resistivity decreases as the temperature decreases, with two distinct temperature regions delimited by \(T \sim 80K\). The second sample exhibits a drastically different temperature dependence: first an increase to a maximum at \(\sim 200K\), and a decrease to a minimum at \(\sim 30K\), then an increase with a hint of saturation below 4K. However, both temperature dependences are indicative of two competing effects. From figure 3 one can infer the residual resistivity ratios, defined as \(\rho(300K)/\rho(4K)\), for the two compositions: 6 for \(\text{Bi}_2\text{Te}_3 + 0.5\%\text{Sn} + 0.05\%\text{SbI}_3\) and 0.6 for \(\text{Bi}_2\text{Te}_3 + 0.5\%\text{Sn} + 0.1\%\text{SbI}_3\). For the latter composition sample, room temperature Hall Effect measurement results give \(R_H = 2.6 \times 10^{-7}\text{Volt m}^3/\text{Amp Weber}\), carrier concentration \(p = 2.4 \times 10^{25}\text{m}^{-3}\) and mobility \(\mu = 0.0023\text{m}^2/\text{Volt sec}\).

![Figure 4](image4.png)

![Figure 5](image5.png)

Figure 4. Magneto-resistance for both compositions at \(T = 8K\).

Figure 5. Magneto-resistance for both compositions at \(T = 4K\).

Figures 4 and 5 depict the resistance variation with applied magnetic field, \(0 < H < 8T\),
for the two compositions at $T = 8\text{K}$ and $T = 4\text{K}$, respectively. The data is for field ramping up and down at a maximum rate of 0.5T-per-minute. As can be seen, both graphs show little or no hysteresis, as well as, a positive magneto-resistance with a quadratic field dependence but opposite curvatures. The magneto-resistance for metal-like sample (#97) does not show any oscillation with the magnetic field down to 4K. However, the second sample (#98) exhibits quantum oscillations for $H \geq 4\text{T}$ at 8K and for $H \geq 2.5\text{T}$ at 4K. Analysis of figures 4 and 5 allows for quantification of the same period of oscillations ($0.1\text{T}^{-1}$) and an increasing amplitude as the temperature decreases [3].

4. Discussion

As can be seen from Figures 3-5, additional doping with I considerably changes the electro-physical properties of $\text{Bi}_2\text{Te}_3: \text{Sn}$ crystals. The samples show different behaviour of resistivity both with temperature, $T$ and with magnetic field, $H$. Sample #97 shows a pronounced dependence of resistivity both vs $T$ and $H$, which is characteristic for metals and highly degenerate semiconductors. They are characterized by the absence of quasi-local states and $E_F$ is located outside of the $\text{Sn}$ band. Because of that the magnetoresistance does not saturate at high fields, as in all metals, which is explained by inhomogeneities of $\text{Bi}_2\text{Te}_3$. Sample #98 shows a dependence of resistivity both vs $T$ and $B$ that is characteristic for semiconductors and the quantum oscillations of Shubnikov-de-Haas (SdH) are observed (in the same range of magnetic field as for the sample #97). It can be seen from Figures 4 and 5 that, for sample #98, the non-oscillating part of $\rho_{xx}(H_z)$ tends to saturate, and therefore can be described by the equation [4]

$$\frac{R(H)}{R_0} = \frac{\rho(H)}{\rho_0} = \frac{1 + (R_0\sigma_0 H)^2/f_{\parallel}}{1 + (R_0\sigma_0 H)^2}$$

from where it can be seen that a Hall factor, $f_{\parallel}$, has an approximate value of $\sim 0.3$. Hall factor in these materials is highly influenced by the anisotropy of effective mass and the orientation of the energy ellipsoids with respect to crystallographic axis. Neglecting the temperature dependence of the Hall factor, which depends on scattering mechanism and the degeneracy factor, we could estimate the concentration of holes at the Fermi level as $p_F = 7.2 \times 10^{24}\text{m}^{-3}$.

The observed quantum oscillations is a demonstration of excellent spatial homogeneity of electrical properties of quasi-local states of $\text{Sn}$ and one can be conclude that, in this case, the Fermi level is located within the $\text{Sn}$ band which is partially filled. In addition, the temperature dependence of resistivity of sample #98 shows two mechanisms of conductivity: zone conductivity by the VZ and hopping conductivity by $\text{Sn}$ states.

5. Conclusion

Introducing additional iodine impurity into $\text{Bi}_2\text{Te}_3 : \text{Sn}$ is an effective method for changing the location of $E_F$ and altering the character of the conductivity and its dependence on temperature and applied magnetic field.

Acknowledgments

One of the authors (MZT) wishes to acknowledge support and encouragement by the Department of Physics, The College at Brockport, State University of New York.

References

[1] Zhitinskaya M K, Nemov S A and Svechnikova T E 1997 *Semiconductors* **31** 375
[2] Burin P P, Pfeiderer C 1996 *Rev. Sci. Inst.* **67** 4024
[3] Seeger K 2002 *Semiconductor Physics: An introduction* (8th Edition, Springer)
[4] Laiho R, Nemov S A, Lashkul A V, Lhderanta E, Svechnikova T E and Dvornik D S 2007 *Semiconductors* **41** 546