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EFFECT OF EXCESS Bi ON D.C.CONDUCTIVITY MEASUREMENTS OF POLYCRYSTALLINE THIN FILMS OF $Bi_X Se_{1-X}$

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ABSTRACT

D.C. conductivity of thin polycrystalline films of Bismuth Selenide grown from stoichiometric and from bismuth excess charges are studied as one of the important electrical properties of the film. The high and low temperature conductivity data has been analyzed and the effect of excess Bi was studied. An energy band model has also been suggested for this case.

KEY WORDS ***d.c. conductivity, polycrystalline, stoichiometric, electrical***

1 INTRODUCTION

The paper reports the experimental results on d.c. conductivity measurements on polycrystalline thin films of $Bi_x Se_{1-x}$ as a function of temperature and composition. The various transport parameters namely activation energies pre exponential factors and Mott's parameters have been calculated. From the analysis of the data, the charge transport mechanism in this polycrystalline semiconducting system has been identified.

2.0 MEASUREMENT OF THE D.C. CONDUCTIVITY

The d,c. conductivity of various samples was measured by using Vander Pauw technique.The method is explained with the help of fig.1

If a current (I) flows from E to F then a voltage E F drop (V) across G and H gives the resistance R as Fig. 1 (b)

$$R_{EF,GH} = \frac{V_{GH}}{I_{EF}} \tag{2.1}$$

And if current IFG is passed from F to G then a voltage drop (VHE) between the contact H and E gives the resistance

$$R_{FG,HE} = \frac{V_{HE}}{I_{FG}} \tag{2.2}$$

Vander-pauw have predicted that resistivity "p" of the sample obeys the relation.

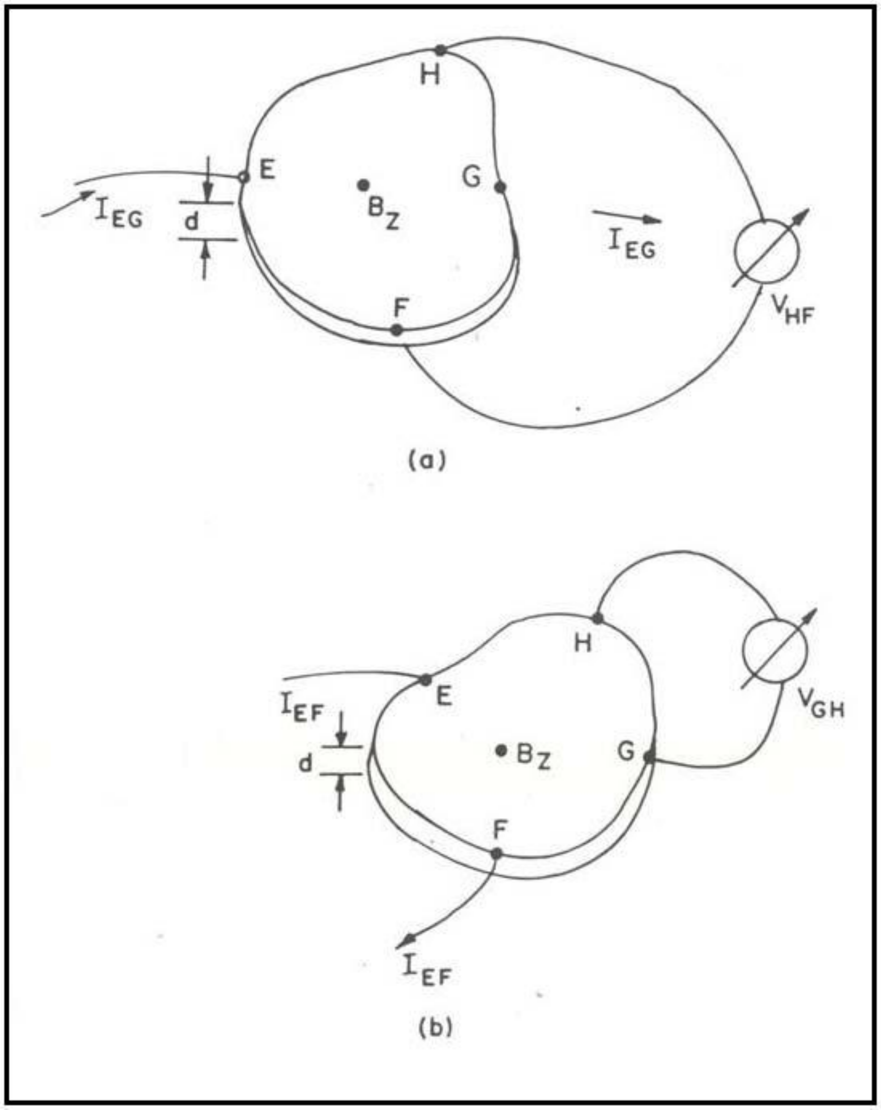


Fig. 1 Vander Pauw technique for the measurement of (a) Hall coefficient; (b) D.C. conductivity.

$$\exp(-\frac{\pi d}{\rho}R_{EF,GH})+\exp(-\frac{\pi d}{\rho}R_{FG,HE})=1 \qquad (2.3)$$

Where ‘d’is the thickness of the sample.

This equation (2.3) cannot be solved for analytically. However, for the contacts possessing a line of symmetry i.e.

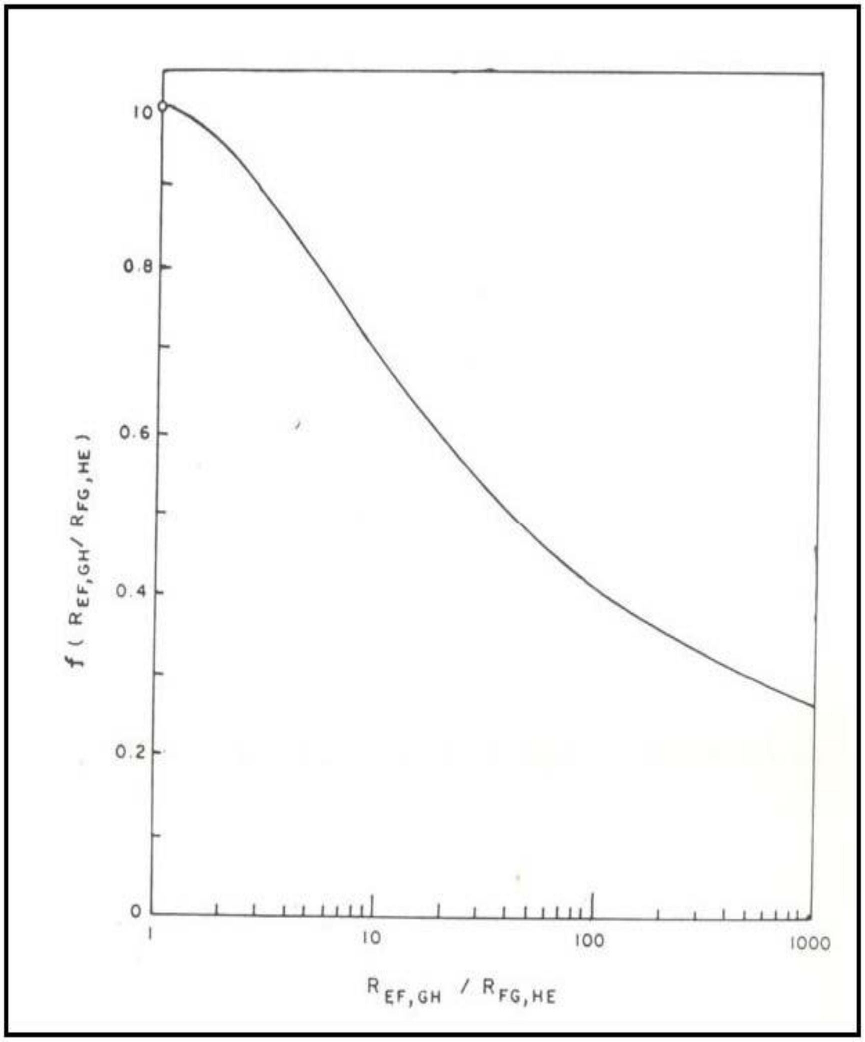


Fig.2. Vander Pauw Factor

$R_{EF,GH} = R_{FG,HE}$

Then equation (2.3) Yields

(2.4)

When, there is no symmetry of the contacts, and then resistivity is given by

$$\rho = \frac{\pi d}{Ln_2} \frac{(R_{EF,GH} + R_{FG,HE})}{2} . f(\frac{R_{EF,GH}}{R_{FG,HE}}) \quad (2.5)$$

$$\rho = -\frac{\pi d}{Ln_2} R_{EF,GH}$$

$R_{EF,GH} / R_{FG,HE}$

here f' is the function which depends on the ration . The variation of ‘f ' as function of ratio $R_{EF,GH}$ and $R_{FG,HE}$ is shown in Fig. 2..

The conductivity have been estimated by using the relation

$$\sigma = \frac{1}{\rho} \tag{2.6}$$

The errors due to thermoelectric effects, which may arise due to thermal gradient present in the samples, were avoided by reversing the current direction. The readings were further noted for two or three currents to avoid errors in the measurements

The observed variation of d.c. conductivity as a function of temperature (160-333 K) for the polycrystalline thin films A,B,C,D shown in the figures 3. to 5 A,B.C and D are four Bix Se1-x films having 1%, 2%, 3% and 4% Bi content respectively. To identify the conduction mechanism, the electrical conductivity data are plotted in three different ways in the figures 3., 4 and 5. Fig3. represents lnσ Vs 1000/T, fig. 4 represents lnσ Vs T-1/4 and fig. 5 represents $\ln\sigma\sqrt{T}$ Vs 1000/T. Table III, IV, and V represent the values of these variation respectively. It is seen from fig. 3, that for a given composition the conductivity in the low temperature region increases slowly with the increase of temperature. Above a certain temperature Ts, the increase in conductivity with temperature is exponential. This indicates that as the temperature is increased (above Ts) the conduction mechanism is changing. To confirm Mott's variable range hopping conduction in low temperature region (below Ts), the conductivity data are repotted in Fig. 4 as lnσ Vs T-1/4 it is observed that in the low temperature region (below Ts), the conduction is in accordance with Mott's variable range hopping conduction as lnσ Vs T-1/4. This suggests that conduction mechanisms are different in the low temperature region and high temperature regions. Another important feature which emerges out from these plots (fig .3.) is that the temperature Ts decreases with increasing Bismuth percentage. The high temperature conductivity data has been plotted in fig 5 as $\ln\sigma\sqrt{T}$ Vs 1000/T. The high temperature conductivity data has been analyzed in terms of Seto's [2] model for thermionic emission of carriers over the grain boundaries according to which the conductivity is given by

$$\sigma = \frac{e^2 l n_{av}}{\sqrt{2\pi m^* kT}} \exp - [(E_v - E_F) + e\phi_B]/kT \qquad (3.1)$$

where nav is the average carrier concentration in the samples, l is the average grain size of the sample, m* is the density of the states effective mass of carriers and $E_v - E_F + e\phi_B = E\sigma\ d$ defines the activation energy for the grain boundary limited conductivity.

The values of conductivity activation energy for all the films A, B, C and D are shown in Table II. It is found that the value of Eσ (conductivity activation energy) is decreasing with increase of Bismuth content in the films. The decrease in the values of Eσ with the increase of Bismuth content shows that the grain boundary barrier potential ΦB decreases with the increase of Bismuth concentration.

As mentioned earlier the conduction in the low temperature range is due to variable range hopping (VRH). The expression for VRH conduction as given by Mott [8, 9, 10] is

$$\sigma = \sigma_o \exp[-(\frac{T_o}{T})^{1/4}]$$

υ_{ph}

(3.2)

where the preexponential factor σ0 is given by Lemoine and Mendolia [1,4] as

$$\sigma_0 = 3 \ e^2 \ \upsilon_{ph} [\frac{N(E_F)}{8\pi \ \alpha \ \kappa T}]^{1/2} \qquad (3.3)$$

Here, υ_{ph} , is the Debye frequency $(\cong 3.3 \times 10^{12} Hz)$ ([1] and

$$T_0 = \frac{\lambda \ \alpha^3}{K \ N(E_F)} \qquad (3.4)$$

Here, N (E_F) is the density of states at the Fermi level, is a dimension less constant [3], is the decay constant of the wave function of the localized states near the Fermi level and K is the Boltzman's constant. The values of T_0 calculated from the slopes of ln $\sigma V/s \ T^{-1/4}$ (fig 4) for different composition are presented in Table I. The other two parameters for Mott's variable range hopping namely energy W are calculated and given in Table I. The expressions for R and W are the following [1,5,6,7,11].

$$R = \left[\frac{9}{8\pi\,\alpha\,\kappa T\,N(E_F)}\right]^{1/4} \tag{3.5}$$

And

$$W = \frac{3}{4\pi R^3\ N\,(E_{F)}} \tag{3.6}$$

Simultaneous solutions of eqns [3.3-3.6] yield,

$$N(E_F) = 5.5\times10^{10}\,(\sigma_0)^3\ T_0^{1/2}\ eV^{-1}\ cm^{-3} \tag{3.7}$$

At T=100 K, the expressions of α. And R can be written as

$$\alpha = 64.303\ \sigma_0 T_0^{1/2}\ cm^{-1}\ \text{and}\ R = \left[\frac{41.5634}{\alpha\,N(E_F)}\right]^{1/4} \tag{3.8}$$

Corresponding values of N (E_F) are calculated from eqn. (3.7) and are given in Table I.

It can be seen from this table that T_0 is of the order of 102 - 104 K and density of states near Fermi level is $\simeq (10^{15} - 10^{20}) eV^{-1} cm^{-3}$ wh which are in good agreement with results obtained by others for polycrystalline semiconductor [12,13]. It is also evident from the table that N (E_F) decreases with increase of Bismuth contents. The values of R and W calculated at 100 K are also listed in table I. For variable range hopping conduction Mott required α R >> 1. The present observations are consistent with these. It is further evident from the table I that in these samples average hopping distance ‘R’ increases and hopping energy ‘W’ decreases with the increasing Bismuth content. This means that effect of grain boundaries which is responsible for hopping conduction in the low temperature region is decreasing with Bi contents

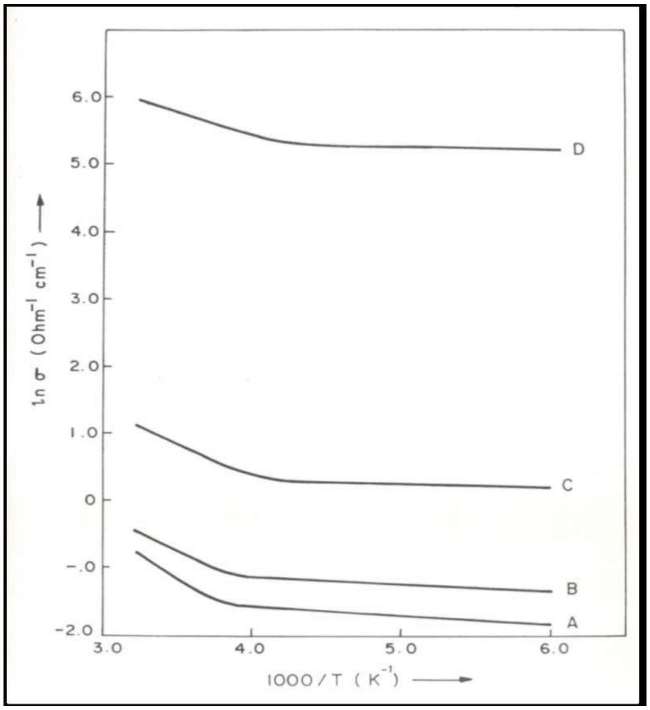


Figure 1

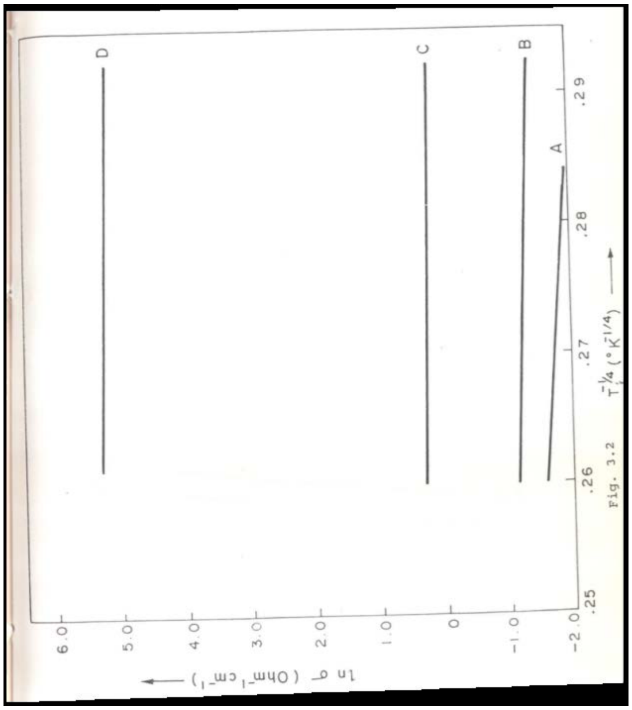
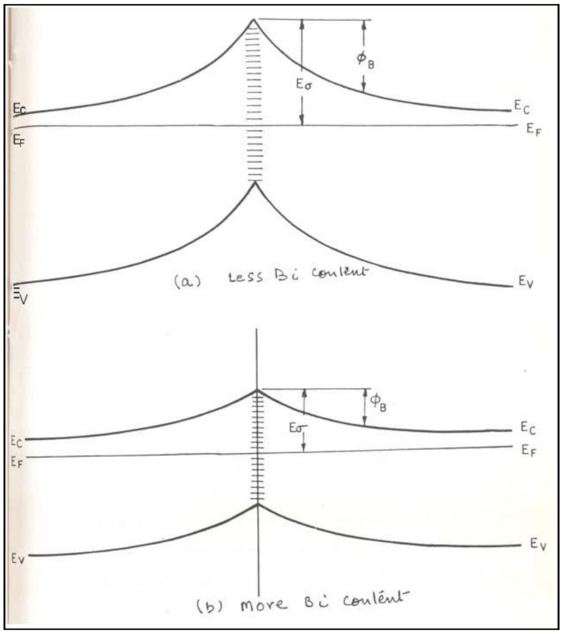


Figure 2



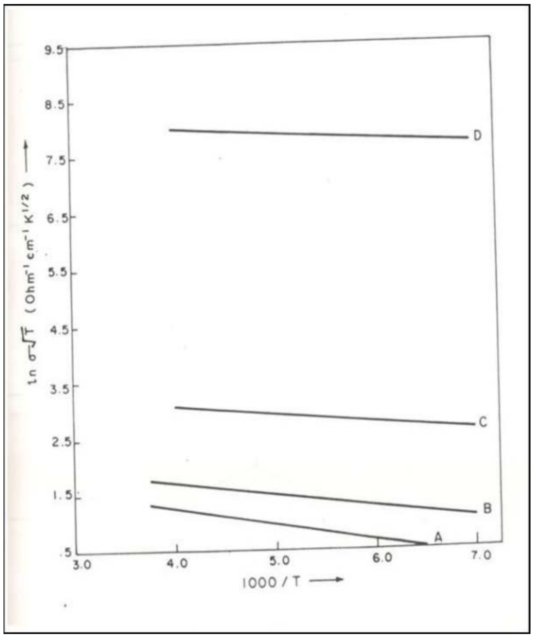


Figure 4 Figure 3

TABLE-I

Values of Conductivity Activation Energy

S.No.	Sample Specification	Eσ (mev)
1.	Film A (1% excess Bi)	137
2.	Film B (2% excess Bi)	110
3.	Film C (3% excess Bi)	86
4.	Film D (4% excess Bi)	31.3

TABLE-2

Values of Various Mott's Parameters

Sample	T_s(K)	T_0(K)	N(E_F) ev^{-1} cm^{-3}	R at 100K (10^{-6} cm)	α R	W at 100 K (mev)
Film A	274	3.84 x10^{4}	4.64 x10^{15}	1.76 x 10^{-5}	1.66	9.45
Film B	259	4.0 x 10^{3}	5.6 x 10^{13}	1.0 x 10^{-4}	1.0	3.21
Film C	222	625	1.7 x 10^{14}	7.3 x 10^{-5}	0.59	3.45
Film D	215	256	1.46 x 10^{20}	8.4 x 10^{-7}	0.47	276

It may be mentioned that To/T represents the degree of disorder in the material [13]. It is the ratio of characteristic disorder energy to the thermal energy. The values of To for the films with 1% excess Bismuth and 4% of excess Bismuth are found to be 3.84x104 and 2.56 respectively which shows that latter films are less disordered. It may be mentioned that the temperature range in which variable range hopping is predominant in polycrystalline materials depends on the relative size of the grain (2) with respect to the Debye length LD. The Debye length is defined as

$$L_D = \left[\frac{\varepsilon\ \varepsilon_0\ \kappa\ T}{e^2 N}\right]^{1/2}$$

(3.9)

Where the dielectric constant and N is is the doping concentration of the samples. If l is << LD practically the entire grain is depleted and variable range hopping will be effective over a wide range of temperature. On the other hand if l >>LD the thermionic emission process is found to be dominant even at very low temperature [12]. Thus the important features of d.c. conductivity data in the present experiment are as follows

1. D.C. conductivity increases with the increase of Bismuth content.

2. For a given composition d.c. conductivity increases slowly with temperature in low temperature region, but above a certain temperature Ts the increase in conductivity is exponential.

3. The value of Ts is found to decrease with increase of Bi content.

4. T0 decreases with the increase of Bi content in the films.

The interpretation of the present results is that the role of excess Bi is to short the grain boundaries, thus reducing the grain boundary barrier potential Φ_B. A Energy band model has been suggested and illustrated in fig. 6 .A few cases of shortening grain boundaries due to excess metal have been observed in thin films [14] of other semiconductor materials. The hopping conduction mechanism in polycrystalline materials arises in grain boundaries. When a charge carrier is transferred from a negatively charged trap centre below the Fermi level to a neutral trap centre above the Fermi level, a process which requires thermal activation. Further the high activation energy observed at high temperatures corresponds to the excitation of the charge carrier from grain boundaries to the neutral region of the grain.

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