EFFECT OF EXCESS Bi ON ELECTRICAL PROPERTIES OF Bi_xSe_{1-x} POLYCRYSTALLINE THIN FILMS

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ABSTRACT

The electrical transport properties such as d.c.conductivity,HallCoefficient,Hall mobility and Thermoelectric power of polycrystalline thin films of Bi_xSe_{1-x} have been studied from liquid nitrogen to 300 K.The role of excess Bi on grain boundaries and grain boundary potential was discussed and presented with a proposed Energy Band Model

Keywords: D.C.Conductivity, Hallcoefficient, Hall Mobility, Thermoelectric Power, Grain boundary, Grainboundary Potential

I. INTRODUCTION

Bismuth Selenide and its alloys have received considerable attention for their application in thermoelectric power conversion. This material has been used to fabricate Ideal Hall effect magnetometers[1],Thermopiles, Hyper frequency power sensors and wide band radiation detectors[2].Thin films of this materials have been investigated by electrical properties have also been reported by many workers [3,4,5,6].In this work, experimental results like dc. Conductivity, Hall Effect measurements and thermoelectric power for polycrystalline thin films of Bi_xSe_{1-x} have been reported in the temperature range of liquid nitrogen to 300K.

II. EXPERIMENTAL

The polycrystalline thin films of Bismuth selenide of size 21mmx4mm were grown from stoichiometric and 1-4% bismuth excess charge by vacuum evaporation technique under a vacuum of approximately $6{,}665x10^{-4}$Pa onto glass substrate preheated to 250^0C.The film deposition rate was about 1nm/sec.The thickness of each film was monitored using a quartz crystal thickness monitor.The electrical contacts on the films were made by evaporating indium onto the films through a tantalum mask.The standard five probe Putley technique**[**18] was used to measure the Hall coefficient and d.c.conductivity.The films were put in a specially designed vacuum cryostat and acopper constantan thermocouple was used to measure temperature. Thermoelectric power measurements were carried out in metal cell with provision for liquid nitrogen cooling.

III. RESULTS AND DISCUSSION

3.1 D.C.Conductivity

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. representslnσ 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 Bismuthpercentage. 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 [28] 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 [7,8,9] is

$$\sigma = \sigma_O \exp[-(\frac{T_o}{T})^{1/4}] \qquad (3.2)$$

υ_{ph} where the preexponential factor σ_0 is given by Lemoine and Mendolia [10,29] as

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

Here, υ_{ph} , is the Debye frequency $(\cong 3.3\times10^{12}\,\mathrm{Hz})$ ([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, lambda is a dimension less constant [30], alfais 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 [10,11,12,13,14]

$$R = [\frac{9}{8\pi\ \alpha\ kT\ N(E_F)}]^{1/4} \qquad (3.5)$$

And

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

Simultaneous solutions of eqns [3.3-3.6] yield,

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

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

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

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 $\simeq (10^{15}-10^{20}) eV^{-1}cm^{-3}$ wł which are in good agreement with results obtained by others for polycrystalline semiconductor [15,16]. 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

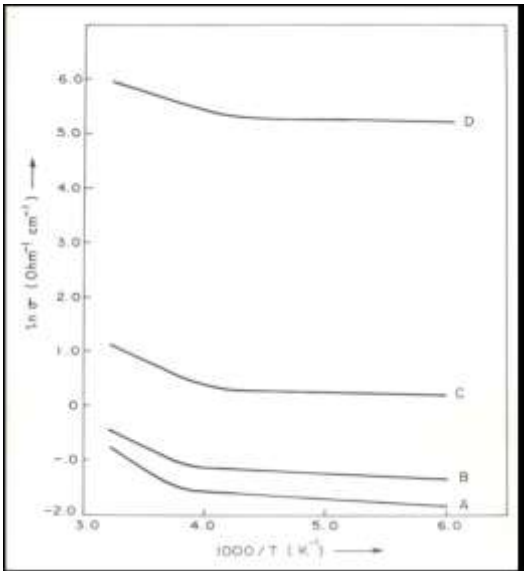


Figure 1

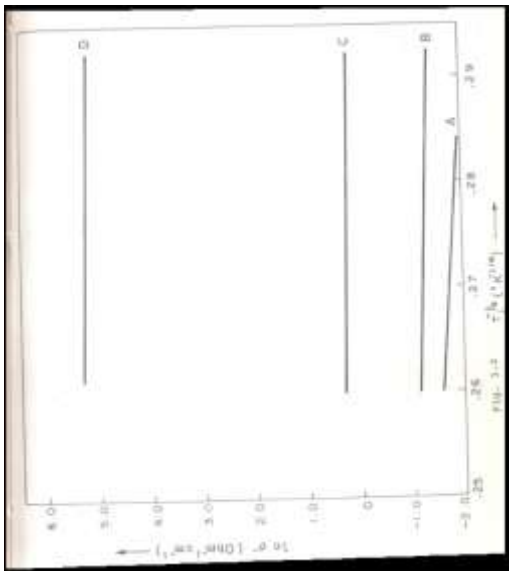
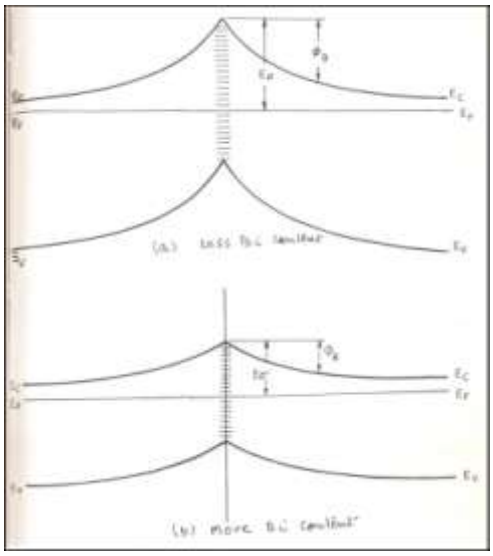


Figure 2



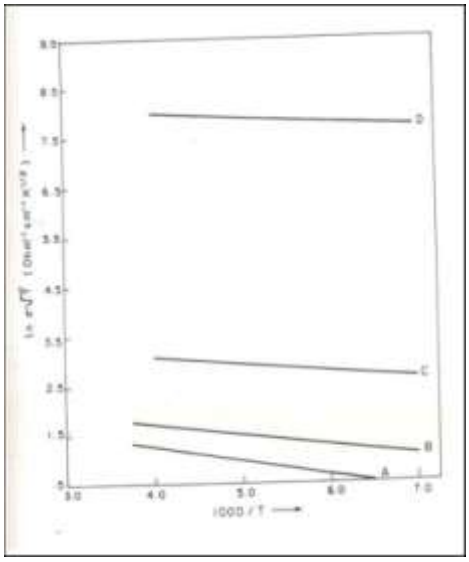


Figure 4 **Figure 3**

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	3.84×10^4	4.64×10^{15}	1.76×10^{-5}	1.66	9.45
Film B	259	4.0×10^3	5.6×10^{13}	1.0×10^{-4}	1.0	3.21
Film C	222	625	1.7×10^{14}	7.3×10^{-5}	0.59	3.45
Film D	215	256	1.46×10^{20}	8.4×10^{-7}	0.47	276

It may be mentioned that To/T represents the degree of disorder in the material [16]. 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

$$L_D = \left[\frac{\varepsilon\, \varepsilon_0\, K\, T}{e^2 N}\right]^{1/2} \qquad (3.9)$$

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 [15]. 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.

4.2 Hall Measurements

The variation of the Hall coefficient with temperature (log R_H Vs 10^3/T) for the films A,B,C and D having 1%, 2%, 3% and 4%. Bi content is shown in figure.3. The values of R_H for different films A,B,C and D is shown Table I. It is observed from this figure that R_H decreases with the increasing content of Bi in $Bi_x Se_{1-x}$ thin films. This signifies that there occurs an increase in the carrier concentration with the increase of Bismuth content. It is found that in all the films A,B,C and D, there is a similarity in the behavior of R_H with temperature. In the low temperature region, the value of R_H with temperature. In the low temperature region, the value of R_H is independent of temperature, which is a typical characteristic of a nearly extrinsic degenerate compound semiconductor [19]. In the high temperature region (>200K), it is observed that there is decrease in R_H with the increase of temperature. This is due to the fact that in the high temperature, the carriers in these films are activated from the grain boundary region to the neutral region of the grain. The observed increase of carrier concentration with the increase of excess Bismuth content further suggests the shortening of grain boundary due to excess Bismuth and supports the conclusions drawn from the conductivity data.

The variation of Hall mobility with temperature (log μ_H Vs 10^3/T) for all the films A,B,C and D with different Bismuth content are shown in fig. 4. The mobility temperature variation for the films having 1% Bi content and 2%. Bi content is characteristic of a typical polycrystalline material. The slow increase of mobility with temperature below 200 K is observed for these films. The result is consistent with the conclusion drawn from the conductivity data viz, the charge carriers are trapped in grain boundaries. The faster increases of mobility temperature variation observed in the high temperature region is due thermionic emission to transfer of charge carriers from grain boundaries to the grain.

In order to estimate the grain boundary barrier potential the high temperature mobility data has been analyzed in terms of Seto's model [20] according to which the mobility is given by the relation.

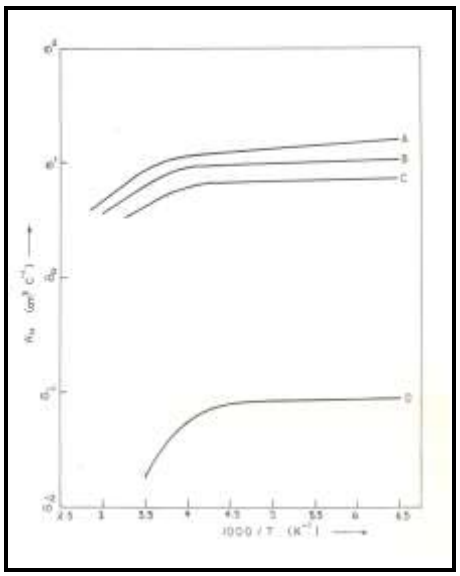


Fig. 3

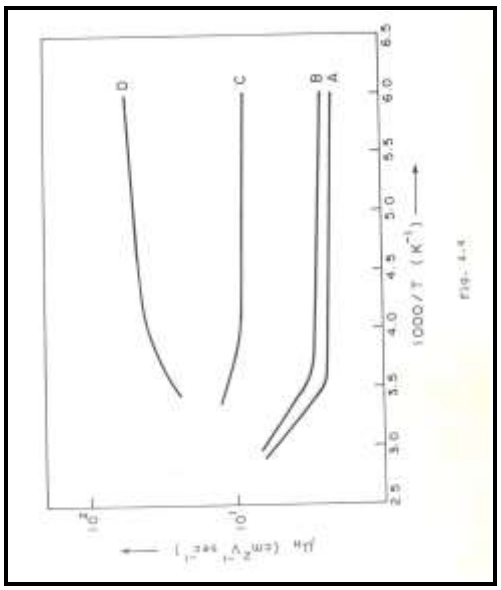


Fig. 4

$$\mu = \mu_0 \exp[-\tfrac{e\phi_B}{KT}]$$

The term u_q depends on the average grain size (l) according to the relation.

$$\mu_0 = el(\frac{8}{\beta^2 \pi\ km})^{1/2}$$

Where β is a numerical constant, m the effective mass of charge carriers, e is the electron charge, k the Boltzmann constant and the grain boundary barrier potential. The values of grain boundary barrier potential for all the films are shown in table II. The value of grain boundary potential Φ_B for the film A (1% Bi) is found to be 55 meV. The value of Φ_B can be compared with the conductivity activation energy of 137 meV calculated for this film from the conductivity data. It may be mentioned that for a polycrystalline material, the conductivity activation energy can be given by the relation [21,22]

$$E_\sigma = E_n + e\,\phi_B$$

Where Eσ is the conductivity activation energy, E_n the carrier activation energy and $e\Phi_B$ is the grain boundary barrier potential. In the present case the observed values of Eσ and E_n are respectively

Table II

Values of Grain Boundary Barrier Potential (ϕ_B)

Sample Specification	Φ_B(meV)
Bi.01 Se.99	55
Bi.02 Se.98	50
Bi.03 SS.97	25

4.3 Thermoelectric Power

The variation of thermoelectric power (S) with temperature (T) for different compositions (A,B,C and D) of Bi_xSe_{1-x} are shown separately in fig. 3 and combined in fig. 4 respectively. It is observed that thermoelectric power is negative throughout the temperature range, for all the samples (A,B,C and D) suggesting that all samples are n type, n-type conductivity maybe due to incorporation of excess selenium in the films [23]. For a given composition of Bi_xSe_{1-x} it is observed that thermoelectric power increases with increasing temperature, attains a maximum value and then decreases with the increase of temperature. This phenomenon may be due to the degenerate nature of the material. Same phenomena have been observed by several workers in bulk Bismuth Telluride [24,25] and bulk Bismuth Selenide [26,27]. It is observed that maxima of thermoelectric power decreases with the increase of Bi content for different Bi_xSe_{1-x} composition. It is also observed from the fig. 4 that maxima of thermoelectric power v/s temperature variation shifts towards the lower temperature with the increase Bi content in Bi_xSe_{1-x} compositions. The interpretation of these results in that effect of excess Bi is to short the grain boundaries thus reducing the grain boundary barrier potential. This reduction the grain

boundary barrier potential is responsible for the decrease in thermoelectric power of Bi_xSe_{1-x} films with increasing content of Bi. These results of thermoelectric power measurement are consistent with the conductivity and Hall mobility data.

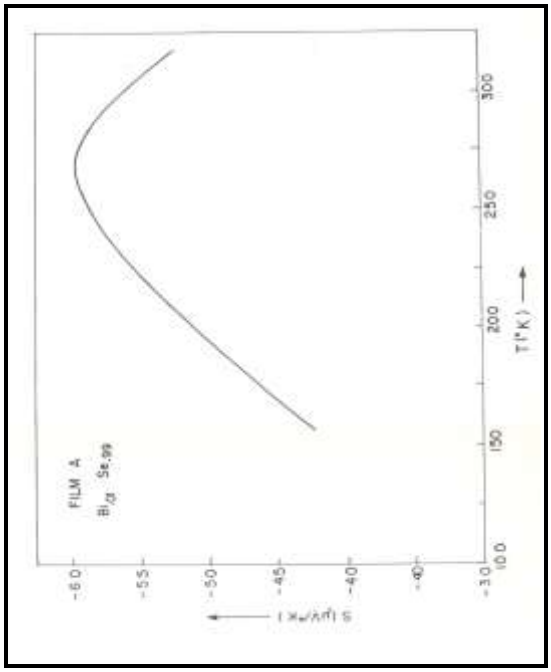


Fig. 3 (a)

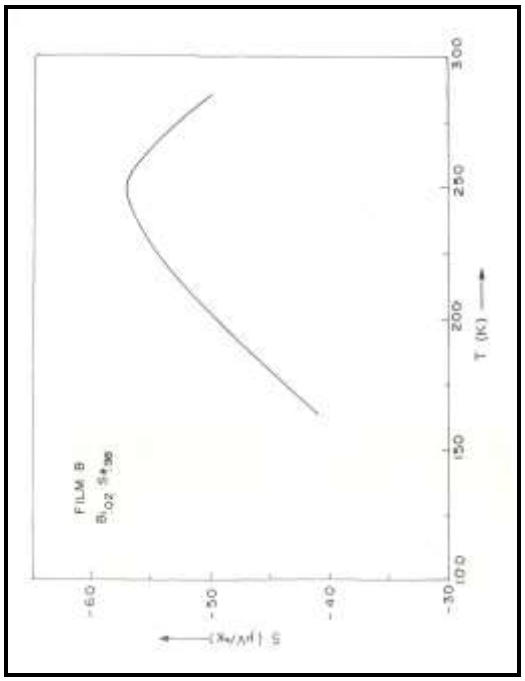


Fig3 (b)

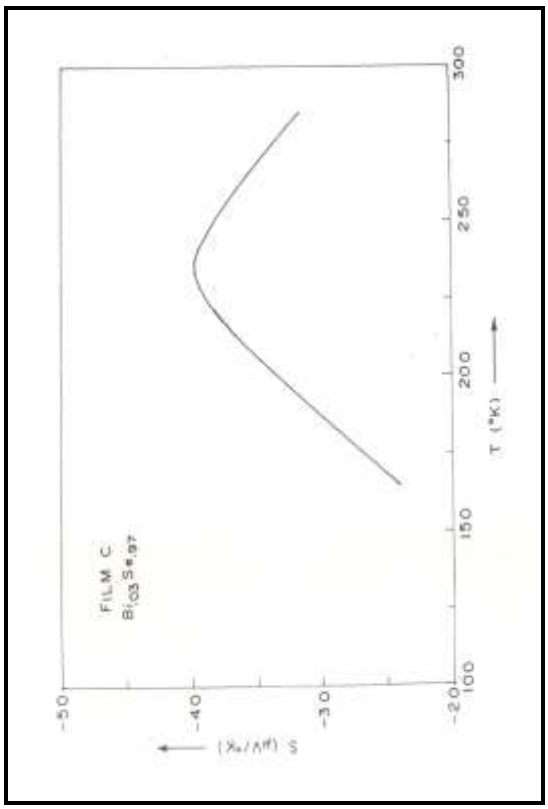


Fig. 3 (c)

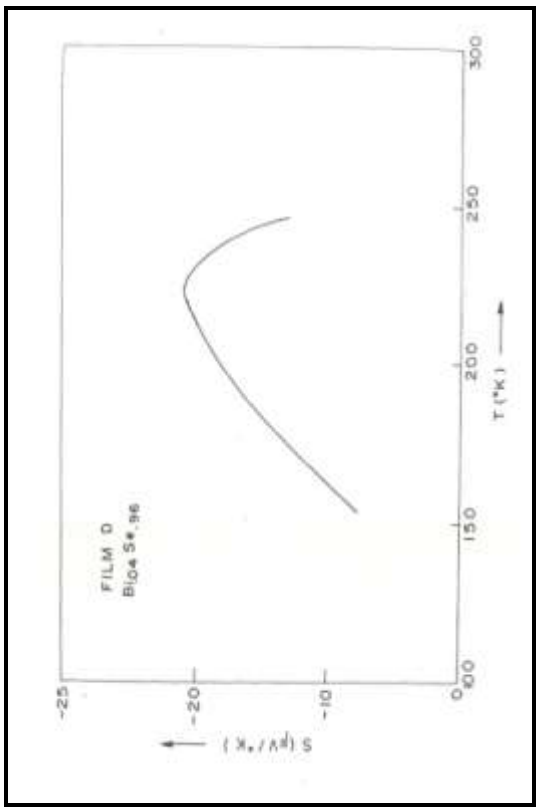


Figure 3(d)

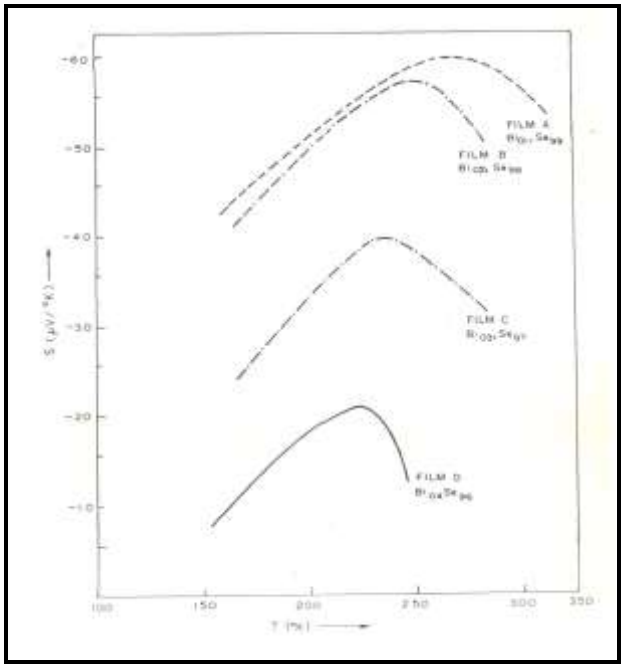


Figure4

V. CONCLUSION

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. 4 under 4.1.A few cases of shortening grain boundaries due to excess metal have been observed in thin films [17] 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.

REFERENCES

[1]. J.A.Woolam,H.A.Beale and I.L.Spain(1973),Rev.Sci.Instrum. 49,434
[2]. A.Boyer,E.Cisse and E.Groubert(1989),Technologies and Applications,APIST and CIAME,Paris,pp 242-247
[3]. A.Goswami and S.S.Kohli(1969),Indian J.Pure Appl.Phys,7,166
[4]. R.N.Bhattacharya, P.Pramanik and E.Mathai(1992),Solid State Commun.83,501
[5]. K.JacobJohn,B.Pradeep and Elizabeth Mathai(1993), 85,10,pp(879-881)
[6]. R.H.Bari and L.A.Patil(2010),Indian Journal of Pure and Applied Physics,48,pp(127-132)
[7]. N.F.Mott. (1969). Conduction in non cystalline materials.Phil. Mag., 19(160), 835-852.
[8]. N.F.Mott. (1972, June).Conduction in non crystalline materials.J.NonCrys.Solids, 8-10, 1-18.
[9]. N.F.Mott, E. (1971). Electronic processes in noncrystalline materials. Oxford: Claredon Press.
[10]. D.Lemoine, J. (1981). Electrical properties of evaporated a-CdTe films.Phy.Letts A, 82(8), 418-422.
[11]. M.Pollak. (1972). A percolian treatment of DC hoping conduction.J.NonCryst.Solids, 8-10, 486.
[12]. Mitra, D. P. (1973). Evaluation of Mott's parameters for Hoping conduction in amorphous Ge,Si and Se-Si. Phy.Rev.Lett, 31, 1000.

[13]. N.F.Mott. (1967). Electrons in disordered structures.Advan.Phy., 16, 49.
[14]. R.M.Hill. (1971). Hoping conduction in amorphous solids. Phy.Mag, 24, 1307.
[15]. V.K. Gandotra, K. F. (1986). Effect of excess Copper on electrical properties of polycrystalline thin films of CuInSe2.Phy.Stat.Sol(a), 98, 595.
[16]. V.K. Gandotra, K. F. (1987). Effect of excess indium on electrical properties of polycrstalline thin films of CuInSe2.Materials Chemistry and Physics, 15, 535-551.
[17]. Wiedler, H. (1966). Conductivity and electrical conductivity surface difference studies on polycrystalline thin films of CuInTe2. Solid State Elec., 9, 373-383.
[18]. E.H.Putley(1960),The Hall Effect and Semiconductor Physics,NewYork,Dover Publications Inc
[19]. N.B. Hannay, Semiconductors, p. 32, Chapman & Hall, London (1960)
[20]. J.Y.W. Seto, J. Appl. Phy. 46 (1975). 5247.
[21]. R.G. Mankarious, Solid State Electron, 7, 702 (1964)
[22]. L.L. Kazmerski& Y.J. Juang, J. Vac. Sci. Technol. 14, 769 (1977)
[23]. K.G.Gunther, W. a. (1959). In Naturewissenschaften (Vol. 46, p. 319).
[24]. H.J.Goldsmid. (1958). Proc.Phy.Soc, 71, 633. LONDON.
[25]. J.Black, E. a. (1957). J.Phy.Chem.Solids, 2, 240.
[26]. G.R.Hyde, H. a. (1972). Phy.Lett A,41A, 319.
[27]. A.A.Sher, I. a. (1984). Inog Mater, 20, 1109.
[28]. J.Y.W.Seto. (1975). The Electrical properties of polycrystalline silicon films.J.Appl.Phys., 5247-5254.
[29]. M.H.Brodsky(ed). (1985). Topics in Applied Physics, Amorphous Semiconductors.NewYork: Springer Verlag.
[30]. L.L. Kazmerski, M. A. (1976). Cu(In Ga)Se based thin film solar cells. J.Vac-Sci Technol., 139.