EFFECT OF EXCESS Bi ON HALL EFFECT MEASUREMENTS OF $Bi_X\ Se_{1-X}$ THIN FILMS

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ABSTRACT

The temperature dependence of the Hall coefficient and Hall mobility of polycrystalline thin films of BixSe1-x were studied in the temperature range 100-300K to understand the electrical properties of this material.The effect of excess Bi on these properties was also studied and reported.

KEYWORDS ***Hall coefficient, Hall mobility,Polycrystalline***

1.0 INTRODUCTION

Bismuth selenide is a narrow gap semiconductor and has found many applications in the fabrications of Hall Effect devices [1] and thermoelectric power conversion [2]. This material has also been used to fabricate Hyper frequency power sensor, thermopiles and wide band radiation detector [3]. $Bi_x\ Se_{1-x}$ has been investigated mostly in bulk form and a little work has been reported on thin films of this material. In the present investigation, thin films of Bi_xSe_{1-x} have been deposited by a technique referred as CSVT-1, which is very similar to close-spaced vapor transport technique [4]. The suitability of this CSVT-1 technique has already been well-established for the growth of good quality thin films [5,6]. In this technique the process is carried out at relatively high vacuum conditions, the source to substrate distance is of the order of 1-2 cm as compared to close spaced vapor transport technique discussed in literature [7-10]. This method though simple, gives films of reasonably good properties. The main objective of the present work is to study the Hall Effect measurements as basic electrical properties of $Bi_x\ Se_{1-x}$

using polycrystalline thin films of $Bi_x Se_{1-x}$ with varying degree of Bi concentration. Experimental Hall coefficients data of the films for various Bi concentration and Hall mobility measurements are plotted and explained.

2.0 HALL EFFECT AND SIGNIFICANCE

In 1879, E.H. Hall [14] discovered that when a current was passed through a slab of material in the presence of transverse magnetic field, a small potential difference was established in a direction perpendicular to both the current flow and the magnetic field. Thus one can write

$$E_y = R_H . i_x . B_z \quad (.1)$$

Where subscripts indicate the direction in rectangular coordinates and R is called as Hall coefficient. For a strip of rectangular cross-section b x t (Fig. 1) where b

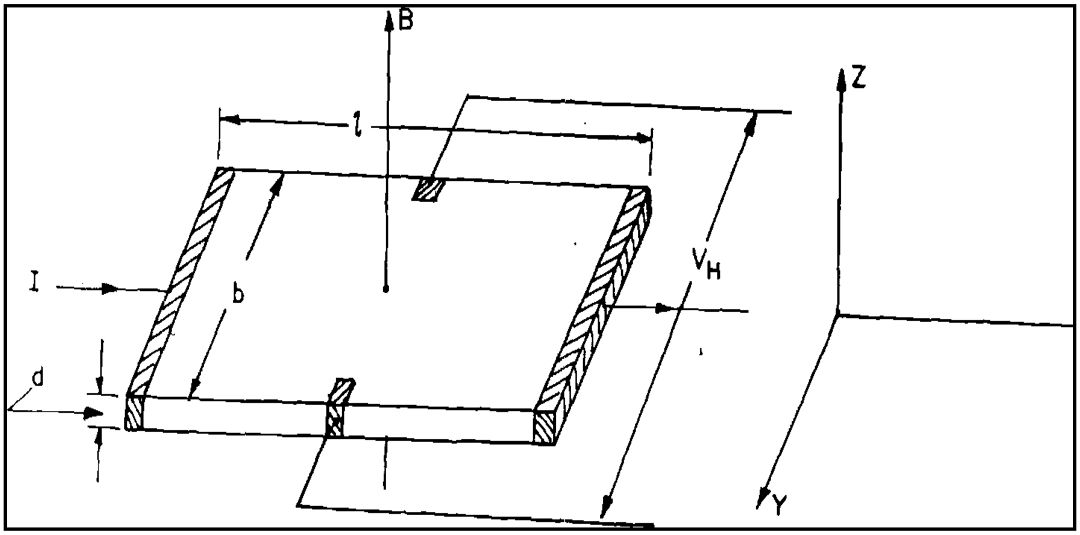

Fig. 1: Diagram depicting the definition of Hall effect.

is the width and t is the thickness, the Hall coefficient may be written as

$$R_H = \frac{V_H}{I} . \frac{t}{B_z} \quad (2)$$

Where $V_H = b. E_y$ is the transverse voltage generated and $I = b.t.I_x$ is total current.

When a charge carrier moving with constant velocity $\vec{V}$ encounters a magnetic field B, it is deflected by Lorentz force $\bar{F}$, in a direction perpendicular to the plane containing the original direction of motion and the direction of field, and is expressed as

$$\bar{F} = e(\bar{V} \times \bar{B}) \quad (3)$$

If the charge carriers are moving in vacuum, they are deflected in the manner expected, but the constraints imposed upon a charge carrier in a solid, prevent the main current stream from being significantly deflected.

If the carriers are flowing along the x-axis and the magnetic field is applied along z-axis, the carriers will experience a force F_y along y-axis (as shown in Fig. 1), which is given by

$$F_y = e.V_x.B_z \quad (4)$$

If this force is balanced by an electric field E_y, then

$$B_z.e.V_x = -e\ E_y \quad (5)$$

The current density i_x can be written as

$$i_x = n.e.v_x \quad (6)$$

Where n is the density of electrons per unit volume.

Hence substituting equation (6) in(5) gives

$$E_y = -\frac{i_x \, . \, B_z}{n\ e} \quad (7)$$

And

$$R_H = -\frac{1}{n.e} \quad (8)$$

Fig. (1) gives the sign of Hall coefficient for n-type carriers.

In deriving equation (8). It has been assumed that all carriers in the conductor have the same uniform velocity. This assumption may be justified for a degenerate semiconductor but it is entirely inapplicable to non-degenerate semiconductors in which the velocity or carriers obeys the Maxwell distribution and a factor of 3π/8 appears on RHS of equation (8). In more rigorous terms, the following expression for R_H is obtained

$$R_H = r_H (1/ne) \tag{9}$$

Where r_H is Hall scattering factor, and its value depends on the geometry of scattering surfaces and the mechanism by which the carriers are scattered. This factor does not depart from unity, for all reasonable assumptions and in general it may be ignored.

The equation (8) shows that the value of Hall voltage is independent of width of the sample. Since the maximum current will be determined by the cross sectional area of the conductor, a plate of minimum thickness and a maximum width will produce the largest transverse voltage V_H. That is why thin plates of the materials are preferred for the Hall measurements.

This definition also assumes that the conductor is infinitely long so that in the absence of magnetic flux, the current density will be uniform. It is well known that if the length is more than four times the width, the error is negligible, but for a square plate the value of V_H is about 0.7 of the value of an infinite strip [15].. Because of this simple relation (8) between the Hall coefficient and carrier concentration, the measurement of Hall coefficient becomes an effective tool in the study of transport parameters. Once the magnitude and sign of Hall coefficient are known, it is easy to determine the concentration and nature of the carriers in a semiconductor. For n-type semiconductors, R_H is negative, while for p-type it is positive.

Besides, simultaneous measurement of electrical conductivity $\sigma = n.e.\mu$, enables us to calculate the mobility of the carriers

$$\mu = R_H.\sigma \tag{10}$$

Combining equations (4.2.9) and (4.2.10), Hall mobility is given by

$$\mu_H = r_H . \mu \tag{11}$$

2.1 HALL EFFECT IN THIN FILMS

Equation (10) is valid for free electron model of bulk material having only one type of current carriers. In thin films it should be modified due to scattering of carriers by the surfaces. At small magnetic fields the modified Hall coefficient can be written as

$$R_{HF} = R_{HB} \quad , \kappa_r > 1 \tag{12}$$

and

$$R_{HF} = R_{HB} . \frac{4}{3} . \frac{1-p}{1+p} . \frac{1}{(\kappa_r (\text{In}(1/\kappa_r))^2} . \kappa_r , p << 1 \tag{13}$$

The expression for mobility follows from equation (10) as

$$\mu_F = \mu_B [1 + \frac{3}{8k_r}(1-p)]^{-1} \quad \kappa_r >> 1 \tag{14}$$

and

$$\mu_F = \mu_B [\ln \frac{1}{8k_r}]^{-1} \quad \kappa_r >> 1 \tag{15}$$

Where subscript 'F'and 'B' refers to films and Bulk respectively.. The theory further predicts an oscillatory behavior of R at very large fields [16].

In general one can consider two types of scattering, the surface and the bulk one, each having its characteristics relaxation time τ_s and τ_1 respectively. The resultant relaxation time

τ_F can be expressed as

$$\frac{1}{\tau_F} = \frac{1}{\tau_B} + \frac{1}{\tau_i} \tag{16}$$

The surface relaxation time τ_s can be estimated by dividing total thickness of the film by mean velocity v as

$$\tau_s = \frac{t}{v} = \frac{t}{\lambda}.\tau_i = \kappa_r \ \tau_i \tag{17}$$

Where λ is the mean free path defined by $\lambda = \tau_i \ v_z$ and $\kappa_r = t/\lambda$ the mean free path is given by

$$\lambda = \mu_i \frac{h}{e} (\tfrac{3}{8\pi} n_i)^{1/2} \tag{18}$$

With μ_i and η_i respectively the mobility and concentration of free carriers in n-type materials.

The average mobility in case of a thin film is taken as

$$\mu_F = \frac{e \ \tau_F}{m^*} \tag{19}$$

in analogy with the corresponding expression for bulk mobility $\mu_i = \frac{e \ \tau_F}{m^*}$ where m* is the effective mass of the carriers. Combining equations (16) and (17), μ_F can be written as

$$\mu_F = \mu_i \left[1 + \frac{1}{k_r} \right]^{-1} \tag{20}$$

showing that mobility decreases as the film thickness decreases while u * u for k » 1. If all the electrons are not scattered diffusely but a fraction ^{x}p' of them is reflected by specular scattering the equation (20) can be modified as

$$\mu_F = \mu_i \left[1 + \frac{(1-p)}{k_r} \right]^{-1} \tag{21}$$

A detailed theory is available in literature [17]. The surface properties and effects have greater significance in semiconductor films, as they have a special influence on their electrical properties due to the fact that the field produced by surface charge penetrates to great depth in the semiconductor and thus influence the electrical transport phenomena. This field causes bending of the energy band at the surface which can be neglected provided the film is having very large thickness or the thickness is small enough compared to the penetration depth of the field i.e.

Debye length $$L_D = \left[\frac{4\pi\varepsilon_0 \varepsilon \kappa T}{e^2 (n_0 + p_0)} \right]^{1/2} \qquad (22)$$

where n_0 and p_0 are the concentrations of electrons and holes respectively in the bulk and ε is the static dielectric constant.

In thick films (t » L_d) the carrier transport is dominated by the size effect and the bending of energy bands due to surface space charge cannot be neglected. If the surface potential drop is denoted by V_s and L_c is the effective charge distance from the surface to the centre of space charge penetration depth, then

$$L_c = \frac{|V_s| L_D}{F_s} \qquad (23)$$

Where V_s is the normalized value of the surface potential drop V_s defined as

$$V_s = e.\, {}^{V_s}\!/_2\, K T \qquad (24)$$

and F_s is the space charge distribution function which decreases rapidly with increasing V_s. If bands bend only slightly (flat band approximation) i.e. V_s is small, then L_c=L_d. The electrons in the bending region are accumulated if the bands are bent downwards (surface accumulation layer), and retarded (surface depletion layer) in case of upward bending, and only those electrons reach the surface which have sufficient energy to surmount the retarding barrier. The kinetic energy of electrons is increased because of the surface potential V through which they drop. Taking into account the above considerations the surface mobility can be written as

$$\mu_s = \frac{\mu_i}{1 + \frac{\lambda}{L_c}(1 - p)(1 + V_s)^{1/2}} \qquad (25)$$

The corresponding expression for the depletion layer is more complex. The expression is further modified as

$$\frac{\mu_s}{\mu_i} = \left[1 + \frac{\lambda (1 - p)}{L_c} \right]^{-1} \quad (26)$$

Where $V_s \rightarrow 0$ i.e. no band and μ_s □ μ_i for large values of V_s. For $\lambda << L_c$ size effect is absent in both accumulation and depletion layers.

The expression for conductivity of thin semiconductor films is the same as in the case of metal films for flat band approximation.

2.2 MEASUREMENT OF THE HALL COEFFICIENT (R_H)

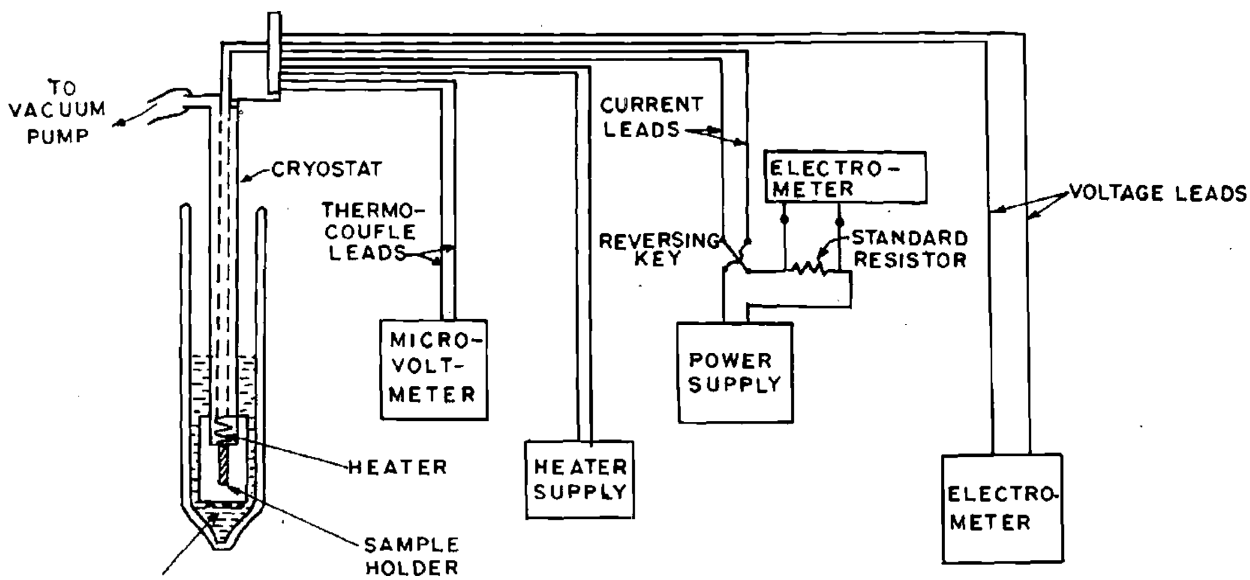

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Fig. 2.: Schematic diagram of the experimental setup.

Using the Vander-pauw method [16,17] for the measurement of the Hall coefficient (Rμ) , a current I was passed through the contacts E and G of the sample as shown in Fig. 3. The voltage drop V_{HF} across the contacts H and F was measured. This voltage drop appears due to slight nonalignment of the contacts. This voltage drop was suppressed to zero by using a compensating circuit consisting of a d.c. potentiometer. Keeping the current constant in the sample, the consequent changes in the voltage drop V_{HF} across the contacts H and F were measured with the application of magnetic field. The Hall coefficient was then calculated using the relation.

$$R_H = \frac{\Delta V_{HF}}{I_{EG}} \cdot \frac{d}{B} \qquad (27)$$

Where‘d’ is the thickness of the film and '$\vec{B}$' is the magnetic field strength.

The observations were repeated over two to three runs. The Hall coefficient was measured at various sample currents with a magnetic field of 5 KG. Errors due to thermomagnetic effects on the

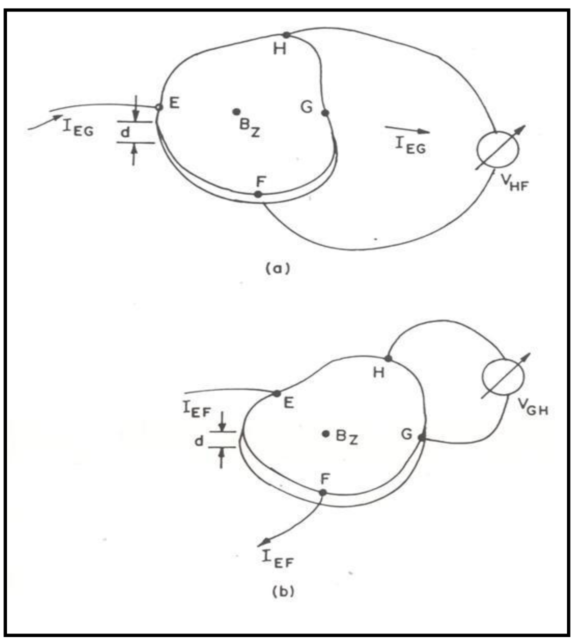

Fig. 3 Vander Pauw technique for the measurement of Hall coefficient

Hall coefficient was eliminated by reversing the directions of the current and magnetic field. Another error which still persists is due to Ettingshausen effect. The effect is a thermal analogue of Hall Effect. A transverse temperature gradient can be produced by the interaction of the magnetic field on the current carriers. This temperature gradient produces Seeback e.m.f. This is reversed when the current or magnetic field is reversed. In semiconductors this error is generally small and the electronic component of the thermal conductance is usually small as compared to the lattice component (unlike metal) [18]. When this condition is satisfied the Ettingshausen error is small than errors due to inhomogeneity and irregularity in the films. Taking into account the errors involved in the measurements of the sample current, the magnetic field and the thickness of the film, the error in R was estimated.

3.0 RESULT AND CONCLUSIONS

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 [18]. 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 analysed in terms of Seto's model [19] according to which the mobility is given by the relation.

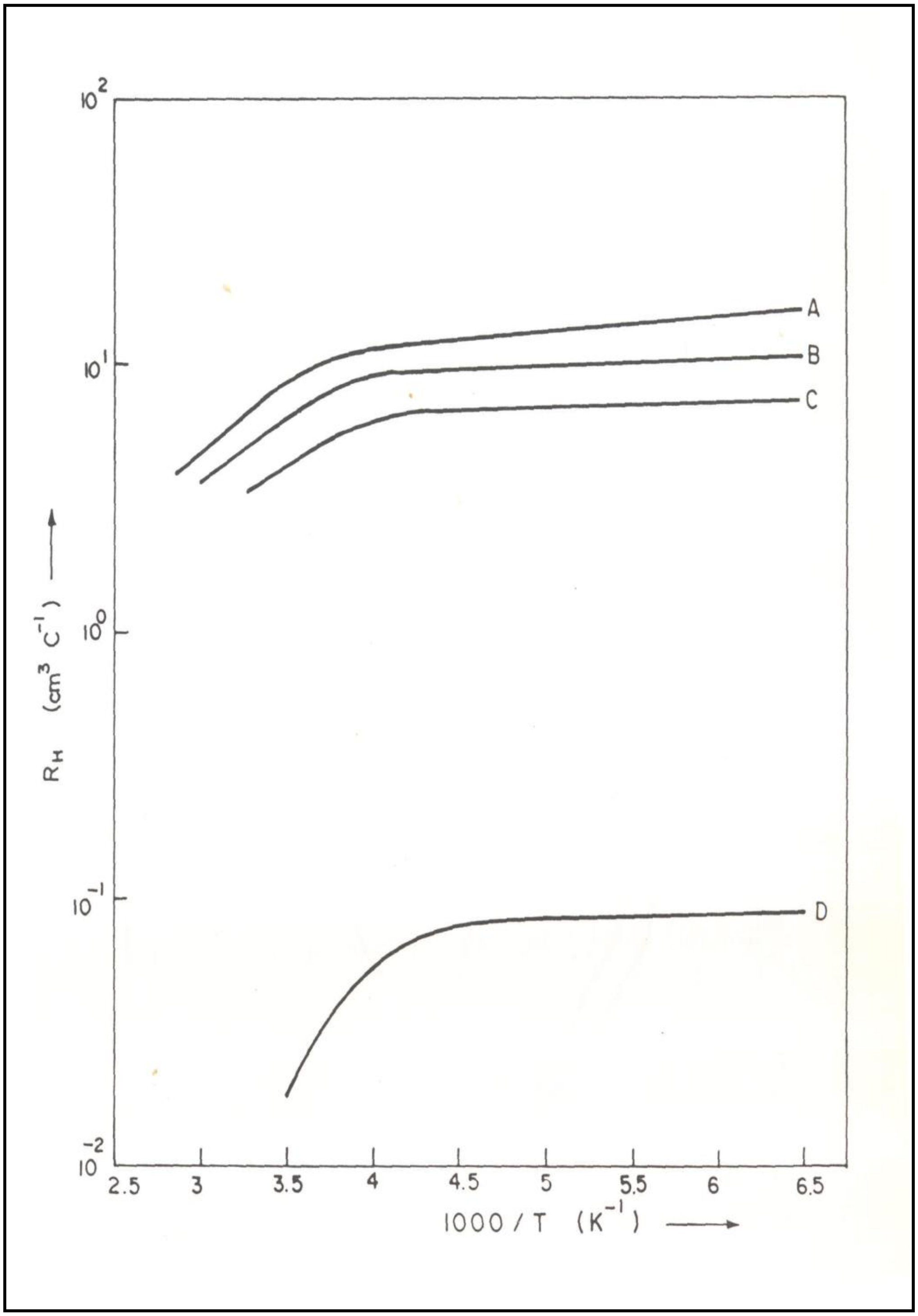

Fig. 3

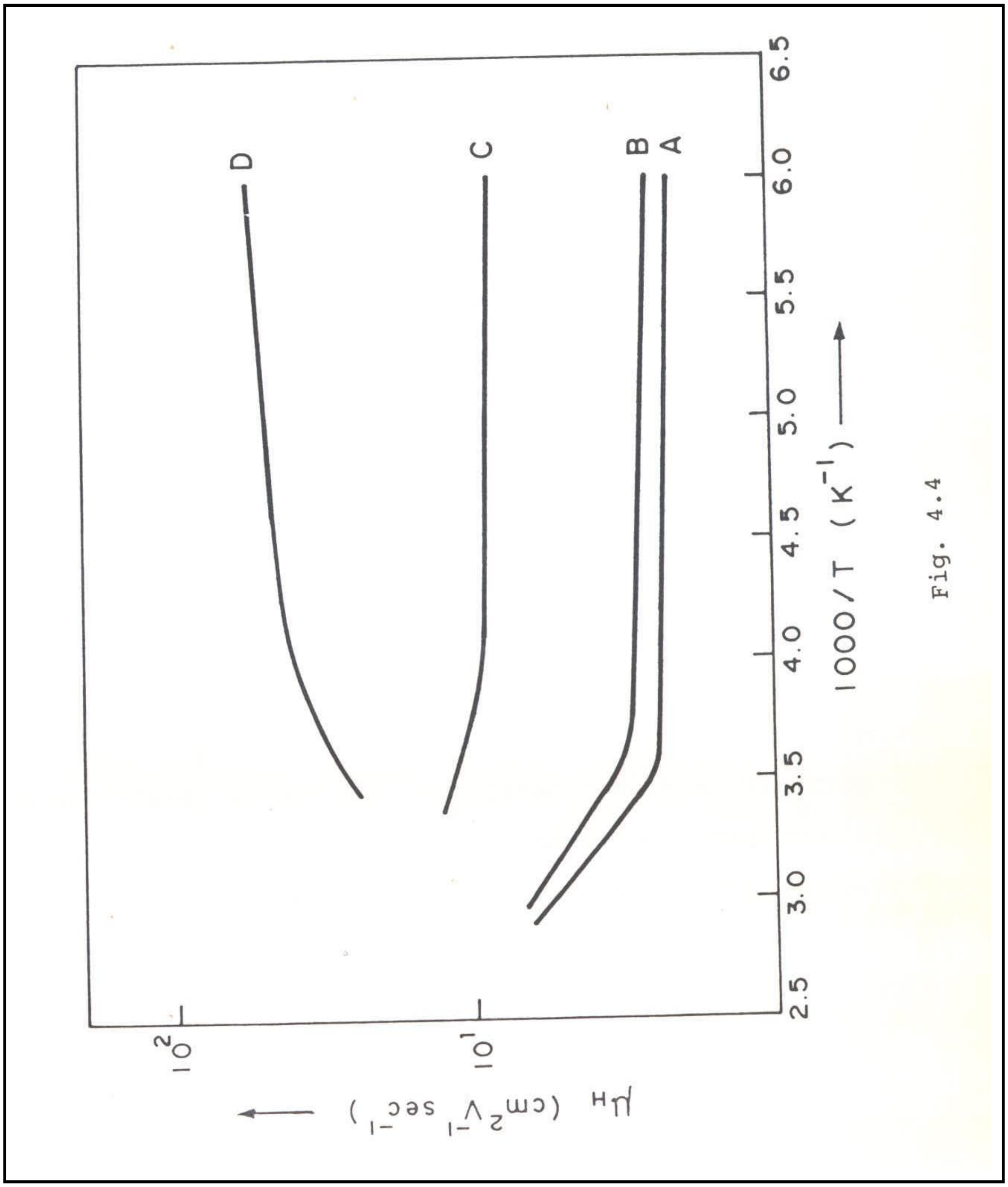
A
B
C
D
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
1000/T (K-1)
10^1
10^2
μH (cm2V-1 sec-1)
Fig. 4.4

Fig. 4

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

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 [20,21,22]

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

where $E\sigma$ 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 $E\sigma$ 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

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