CHAPTER – 9

OPTICAL AND ELECTRICAL PROPERTIES OF THIN FILMS

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Introduction :

The theoretical and experimental investigation of the optical behaviour of solids deal primarily with optical reflection, transmission and absorption properties and their relation to the optical constants, both of the bulk and thin film forms. As a result of these studies, complex multilayer optical device systems with remarkable reflection, antireflection, interference and polarization properties have emerged for both laboratory and industrial applications.

The optical measurement constitutes the most important means of determining the band gap of semiconductors. Optical properties of a thin film differ from those of the bulk. The differences are usually attributed to the microstructure of the films.

There have been a few reports on the optical study on Bi_2Te_3 in bulk and thin film forms. Y Chang [1] et al have studied thin films of Bi_2Te_3 produced by sputtering using targets of the stoichiometric compound. Room temperature carrier concentration and Hall mobility of Bi_2Te_3 films were measured to be 7.2×10^{20} cm^{-3} and 15 cm^2/V-s, respectively. Black et al [2] have studied the optical absorption of Bi_2Te_3 crystals grown by the Bridgman method. Morsey et al [3] have studied optical properties of thermally deposited Bi_2Te_3 thin films in the wavelength range of 2.5 to 10μm and have used transmittance and reflectance spectra to obtain band gap which was found to be about 0.21 eV. Bhatt V.P. et al [4] have reported electrooptic properties of polycrystalline SnSe thin films of different thicknesses deposited at different substrate temperatures. Their results indicate that the resistivity decreases with increase in thickness and substrate temperature. The study of variation of band gap with thickness shows a linear relationship between band gap and inverse square of film thickness. Also it has been observed that the band gap increases with substrate temperature.

V.A.Kutasov [5] et al have sudied electrophysical parameters of epitaxial n-type Bi_2Te_3 films. The growth of films from vapour phase ensures a high carrier density in the condensates because the excess atoms of the components of bismuth telluride are electrically active.

M.S.Rahmankhan et al[6] have measured thermoelectric power, electrical conductivity, TCR and activation energy of Bi_2Te_3 films in the thickness range 600 – 3000 Å. Thermoelectric power, TCR and electrical resistivity are found to show size effects.

Results of optical measurement of $In_xBi_{2-x}Te_3$ Thin Films :

For precision optical measurment, it is desirable to have samples whose surfaces are smooth and optically flat. In the present investigations, thin films of $In_xBi_{2-x}Te_3$ with (x = 0.1 – 0 5) were prepared on glass substrates thoroughly cleaned by a detergent, distilled water and trichloroethylene, under a pressure of 10^{-5} Pa. The film thickness was measured in situ using quartz crystal thickness monitor. The thickness was varied from 400 Å to 3500 Å. A variable power radiant heater placed in the vacuum chamber was used for heating For the optical study a FTIR spectrophotometer (Bomem, Canada) was used. The optical absorption was measured in the wave number range 500 cm^{-1} to 4000cm^{-1} The absorption coefficient was calculated as a function of photon energy from absorptance Vs wavelength curve. The plots of $(\alpha h\nu)^2$ Vs absorptance were used to evaluate optical band gap. Typical plots are shown in Fig.1,2,3, for $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$, and $In_{0.5}Bi_{1.5}Te_3$, thin films of thickness about 1000 Å obtained at 313K. It can be seen that the plot is linear in the region of strong absorptin near the fundamental absorption edge. Thus, the absorption takes place through direct interband transition. The direct band gap obtained by extrapolating the linear part to the zero of the ordinate is also indicated in the figures 1,2,3. The band gap was then evaluated [7-9] for the films of different thicknesses and of different compositions x.

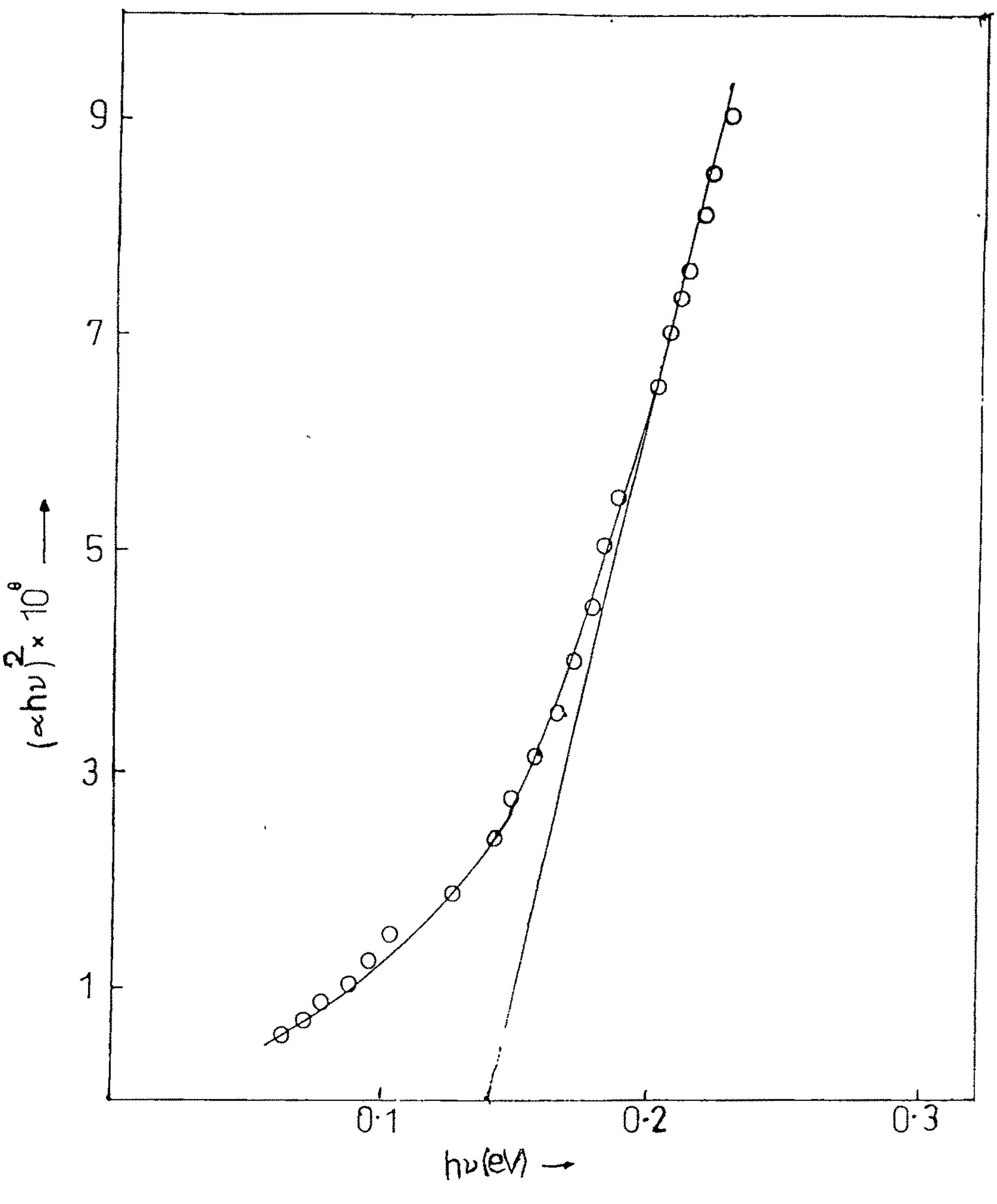

Fig.1 **plot of $(\alpha h\nu)^2$ versus hν : for**

$In_{0.1}Bi_{1.9}Te_3$ thin films

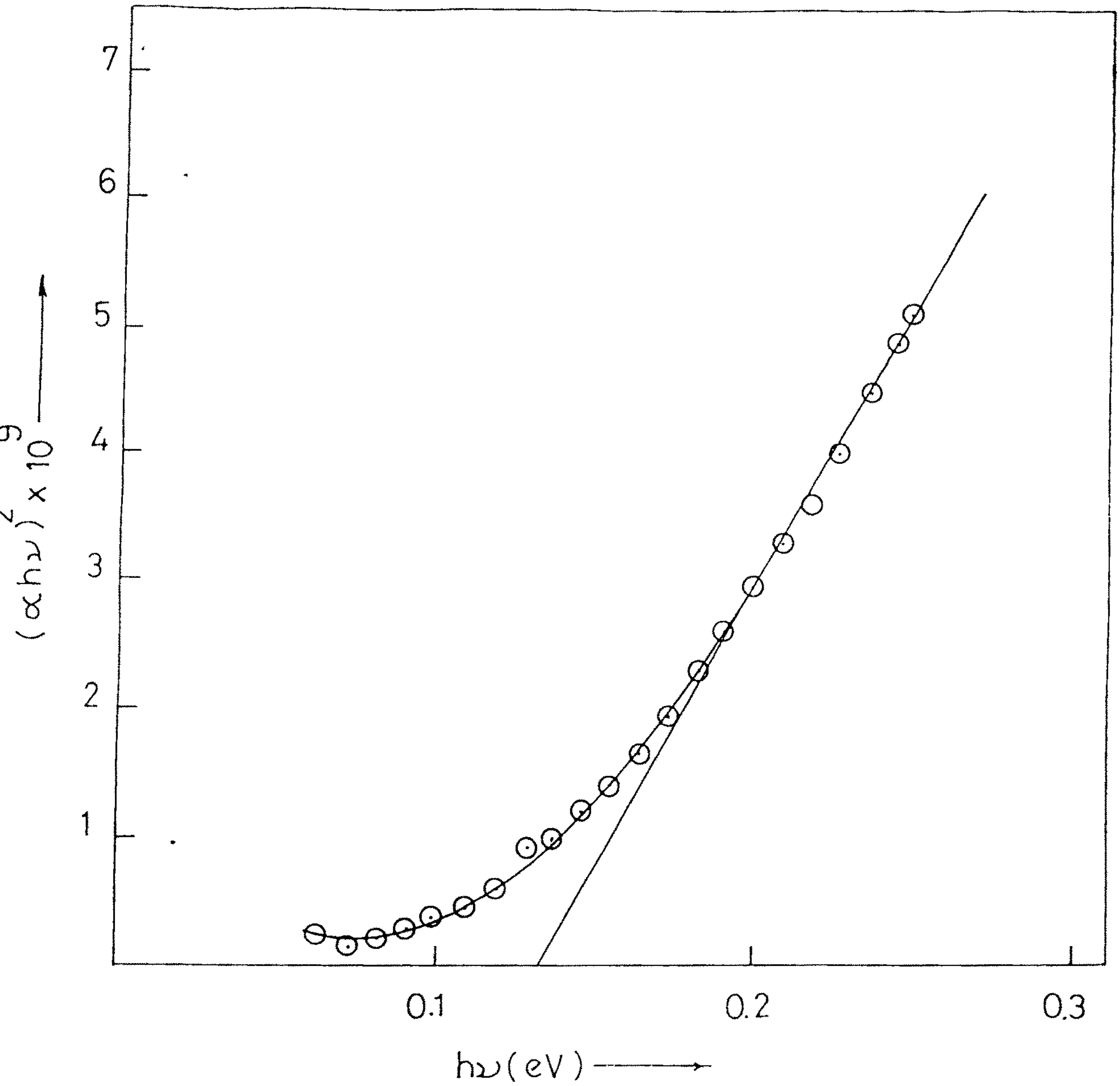

Fig.2 plot of $(\alpha h\nu)^2$ versus $h\nu$ for $In_{0.2}Bi_{1.8}Te_3$ thin films

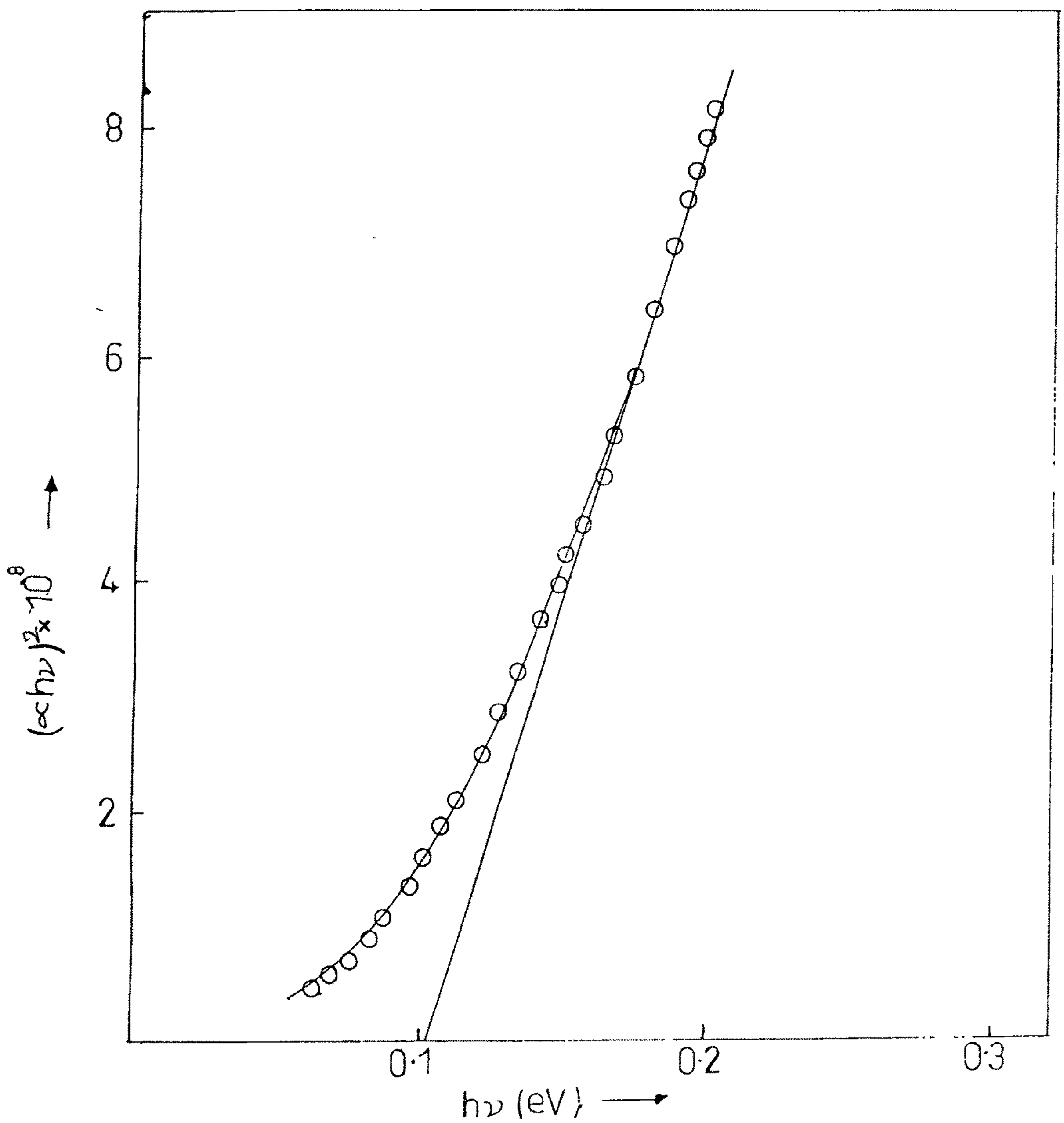

Fig.3 plot of $(\alpha h\nu)^2$ versus hν for $In_{0.5}Bi_{1.5}Te_3$ thin films

It was observed that the band gap changes with thickness within the thickness range used. The band gap 'E_g' plotted versus inverse square of the film thickness 't' is shown in figure 4,5,6 for the three types of films. Such thickness dependence of band gap has been explained in terms of quantum size effect and dislocation density [9-10]. Quantum size effect appears in semiconductor and semimetal films when their thickness is comparable with or smaller than the mean free path or effective de - Broglie wave length of the carriers Because of the small finite thickness of the film, the transverse component of quasimomentm of carrier is quantized and it assumes discrete values along the thickness dimension. The energy spectrum represents a system of discrete levels with the separation between them given by the uncertainty principle The effect of the discrete energy levels on the forbidden gap of a semiconductor has been considered by Sandomiskil [10]. According to him, all levels of the energy spectrum of a semiconductor will be shifted by an amount ΔE In the thin film specimen, provided smearing of energy levels by temperature and diffuse scattering of the carriers at the film surface boundary are not signifiant, this shift will increase the band gap and affect the opticl behaviour of the films. The absorbtion is reduced in thinner films as compared to the case of bulk. ΔE is given by

$$\Delta E = \frac{h^2 \pi^2}{2m^*} \times \frac{1}{t^2}$$

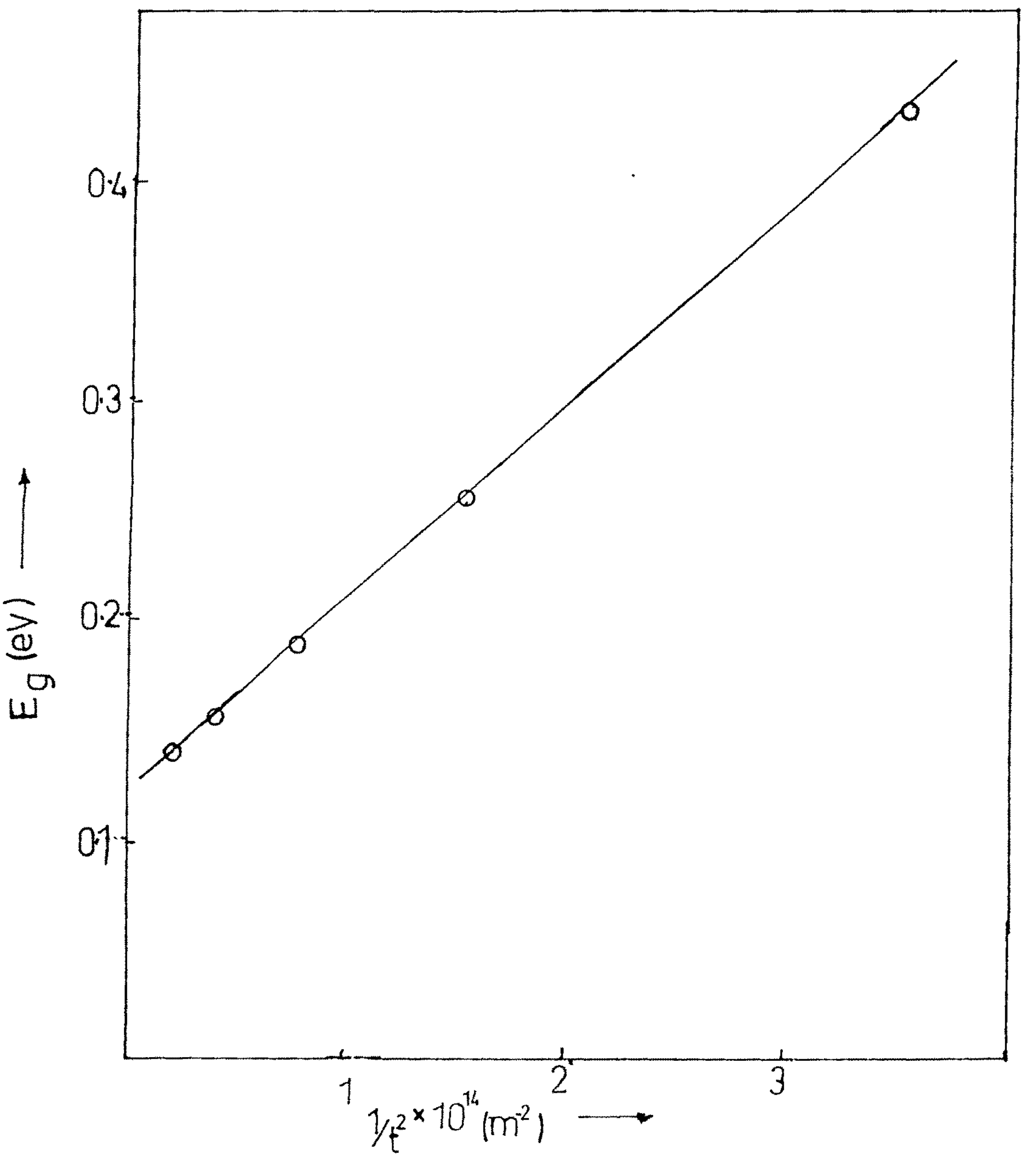

Fig.4 plot of E_g versus $1/t^2$ for $In_{0.1}Bi_{1.9}Te_3$ thin films

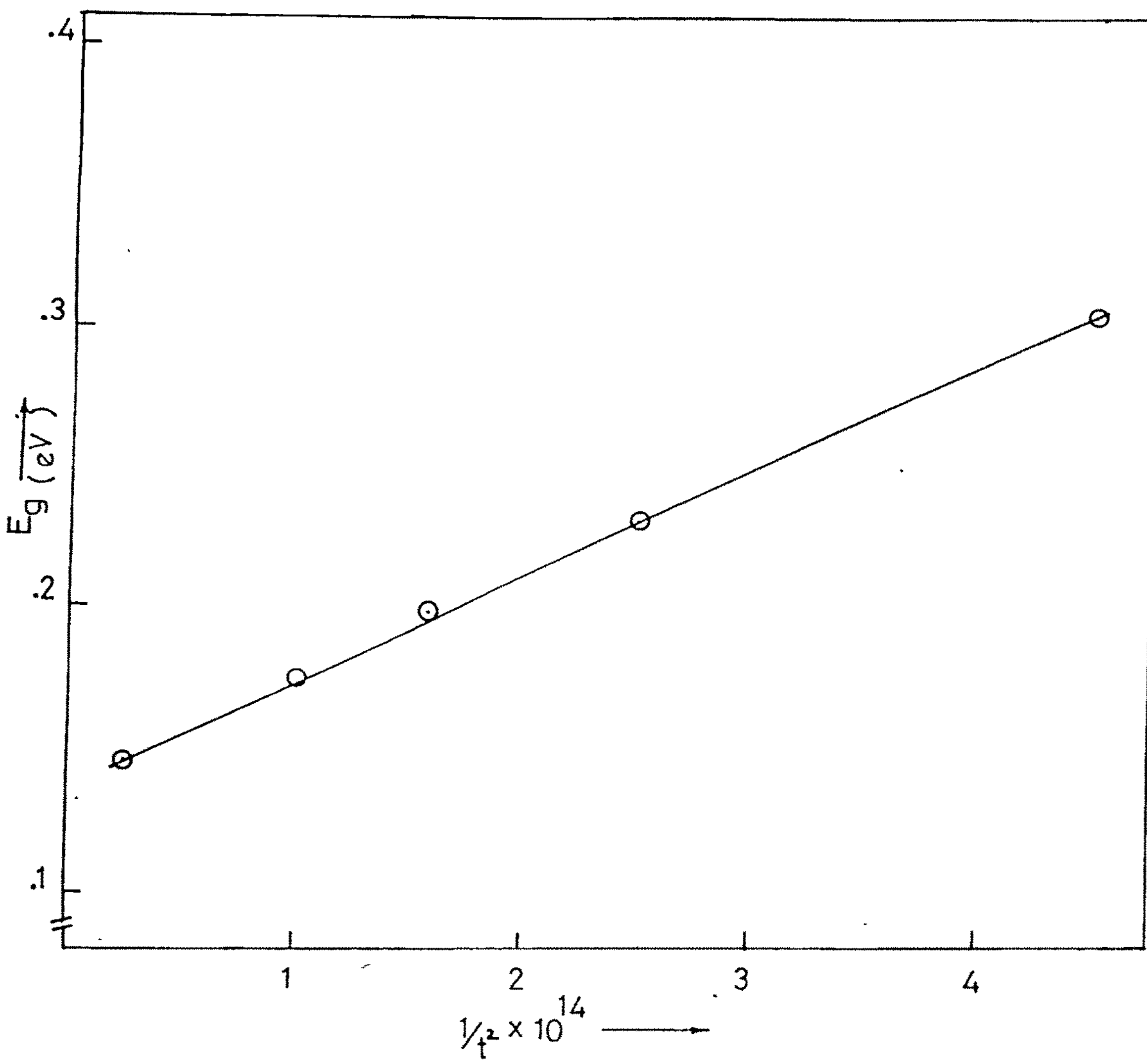

Fig.5 plot of E_g versus $1/t^2$ for $In_{0.2}Bi_{1.8}Te_3$ thin films

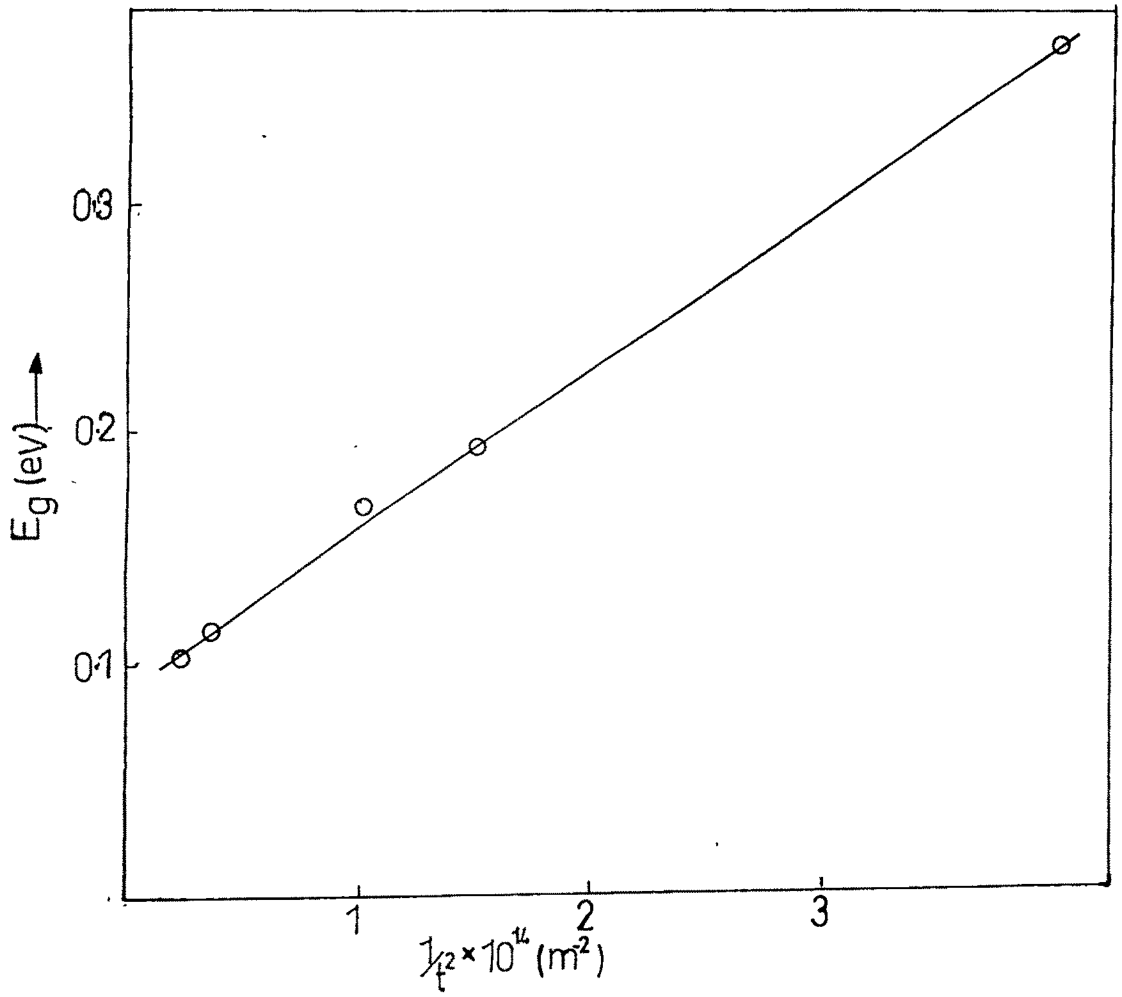

Fig.6 **plot of E_g versus $1/t^2$ for $In_{0.5}Bi_{1.5}Te_3$ thin films**

where,	t	=	thickness of the film
	h	=	Planck's constant
	m^*	=	effective mass of carriers

The plots obtained of E_g versus $1/t^2$ are shown in Fig.4,5 and 6. The straight lines are in agreement with the above relation and imply the quantum size effect operative in the present case.

It is also known that a fairly large number of dislocations are created during the formation of the films and their density increases as the thickness increases upto a particular value beyond which the density is practically constant corresponding to the average bulk value. However, the dependence of dislocation density on thickness has not been quantified and in any case the dependence is complex. There are considerable lattice distrubrances due to dislocations. The disrupted or dangling bonds with their specific charge and the space charge domain that form immediately in the vicinity of the dislocations bear their effects on the band gap with increasing film thickness; the effect of the initial granular structure on the optical properties decreases but is not eliminated completely.Therefore, thickness dependence is still observed although the general behaviour of the optical parameters follow that of the bulk at least qualitatively. In an infinite thick crystal, the electron energy is a multivalued continuous function of the quasimomentum.

The variation of band gap with the crystallite size has been explained by the modified form of Stellar's formula [11]. According to him the increased barrier height is given by

$$E = E_o + c\,[x - fD]^2$$

where,	E_o	=	original barrier height
	C	=	term depending on the density of charge carrier, electronic charge and dielectric constant of the material.
	x	=	barrier width
	D	=	dimension of the grain
	f	=	factor depending upon the charge accumulation and carrier concentraton

It is known from the literature that the grain size is approximately proportional to thickness and hence increases as thickness increases [12]. Hence if we replace D, the grain size in the above expression, by the film thickness t, we find that E in the above expression should be propotional to

$$(x - ft)^2$$

However, in the present observation, we find that the band gap varies inversely as the square of the film thickness and hence it can be concluded that the observed band gap obeys the equation (1). Thus in these bismuth tellurides the quantum size effet is dominant rather than the grain size effect

Effect of substrate temperature on resistivity, carier mobility and carrier concentration of $In_xBi_{2-x}Te_3$ films :

In order to study the effect of the substrate temperature on the electrical parameters such as resistivity and carrier concentration, the samples were prepared under identical conditions by keeping all other parameters constant: the rate of evaporation about 0.5 nms^{-1} and the residual pressure of 10^{-5} Pa. The thickness was varied from 50nm to 200nm range.

The substrate temperature was controlled by the digital temperature controller Digital meters were used for all electrical measurements.

Electrical Resistivity :

A semiconductor is often defined to be a material with an electrical conductivity intermediate between that of an insulator and a metal. The properties of semiconductors which are generally termed as their electrical properties include

1. Electrical Conductivity
2. The Hall coefficient which determines the carrier concentration and type.
3. Hall mobility of the charge carriers

4. Many semiconductors change their resistance when subjected to magnetic field; the effect being known as magnetoresitivity. In this case usually the fractional change of the resistivity $\Delta\rho/\rho_0$ in the magnetic field with respect to zero field value is obtained.

In the case of thin films since the resistance is usually high, van der Pauw [13] method is not practical due to small value of voltage, which usually connot be measured accurately. So instead, the linear four probe method described by Goswami and Ojan [14] [Fig.7] was used in the present study. The sample was prepared in rectangular geometry with pre- evaporated Ag (silver) films as the ohmic electrodes. The length to breadth ratio of the film was kept more than four so as to avoid geometrial influence on the electrical characteristics. The resistivity was calculated using the formula,

$$\rho = \frac{RWa}{l}$$

where, R = resistance of film

l = length of film

W = breadth of film

a = thickness of the film.

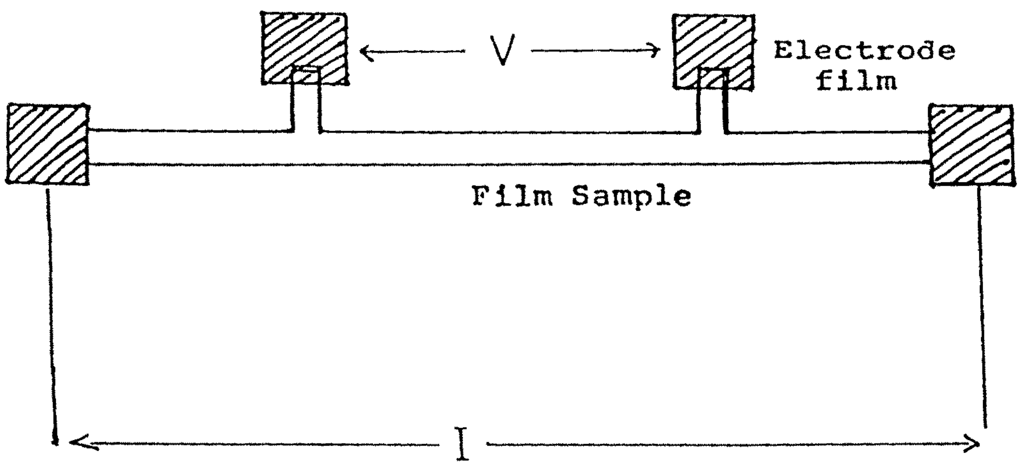

Figure -7 : Linear four probe geometry.

The measurments were carried out on films of different thicknesses at different substrate temperatures. Figures 8 and 9, show the plots of electrical resisti-

vity versus thickness of the film deposited at 150°C and 225°C, for $In_{0.1}Bi_{1.9}Te_3$, $In_{0.5}Bi_{1.5}Te_3$, films. The resistivity of the film is found to decrease with increasing thickness and substrate temperature. It may be due to increase in grain size with increase in substrate temperature. Such a variation in resistivity is explained by Patritz's barrier model [15].

Because the crystallites do not grow sufficiently at low temperatures, the inter crystalline barriers are wide, offering a high resistance to the motion of charge carriers. Whereas, at higer substrate temperatures, large crystallite size is obtained which ultimately decreases the inter crystalline barrier. The charge carriers therefore have to cross comparatively narrow inter crystalline barriers and this results in a decrease of resistivity.

Hall effect measurement :

Hall effect study of $In_{0.1}Bi_{1.9}Te_3$, and $In_{0.5}Bi_{1.5}Te_3$, films was made using the Hall bridge geometry of the samples as shown in Fig.10.

The film dimensions were : width W = 3mm, length L = 20mm with L/w = 6.6 since shorting effect of Hall voltage is negligible only if the ratio exceeds 2.5 [12].The film samples were obtained by depositing $In_xBi_{2-x}Te_3$, with x = 0.1, 0.5

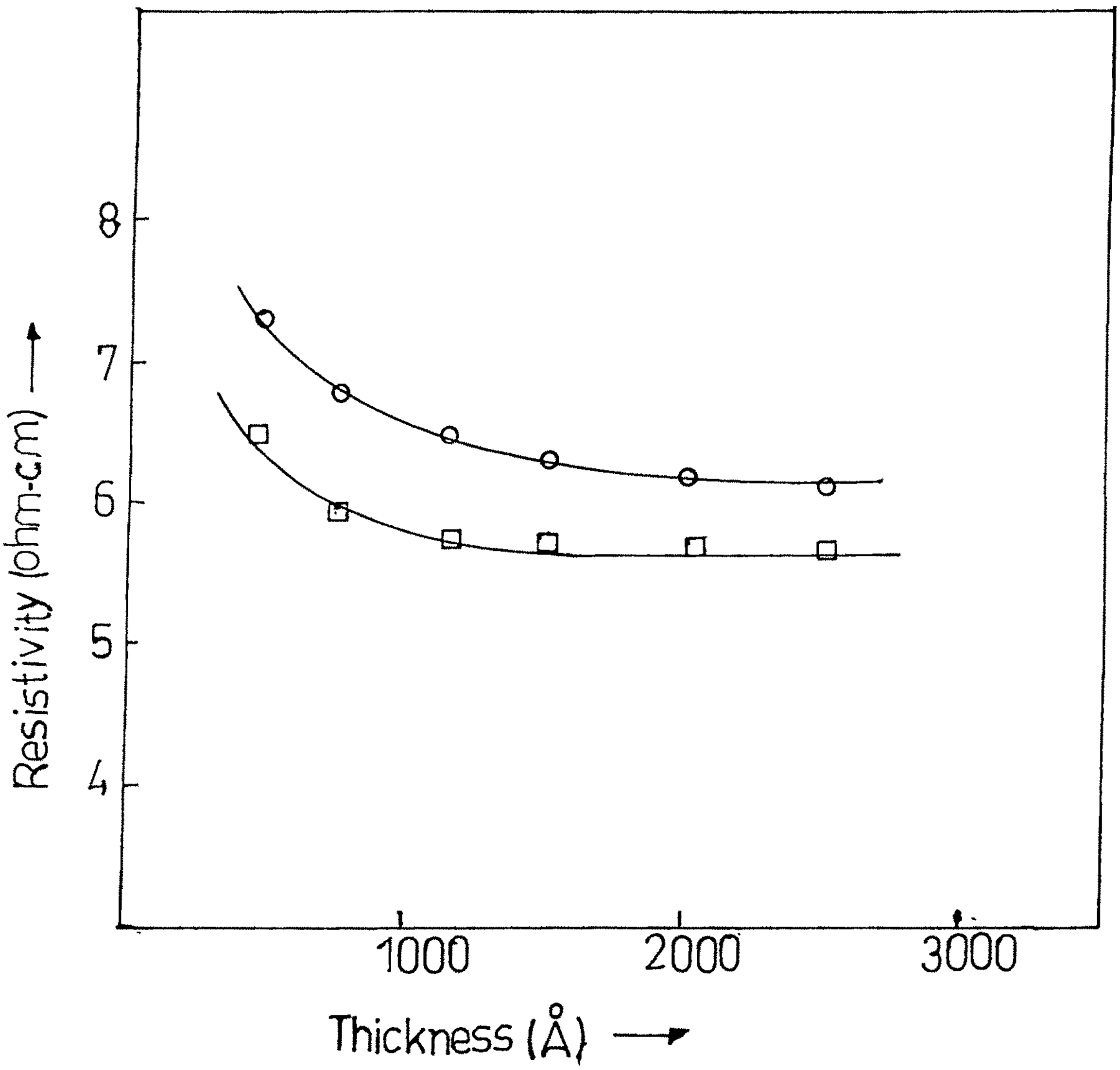

Fig.8 **Plot of electrical resistivity (ρ) versus thickness of the film (t) for $In_{0.1}Bi_{1.9}Te_3$ thin films**

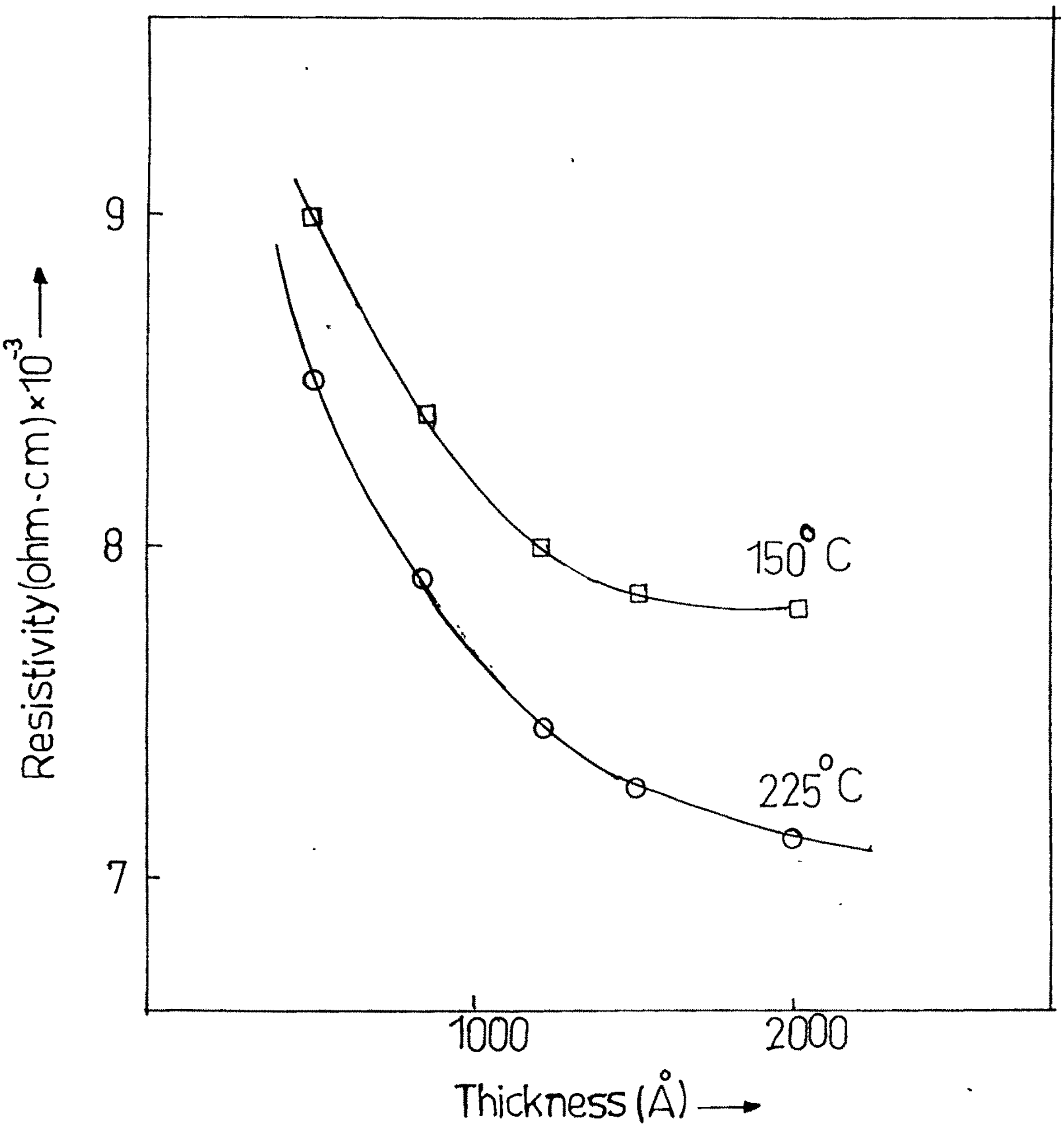

Fig.9 **Plot of electrical resistivity (ρ) versus thickness of the film (t) for $In_{0.5}Bi_{1.5}Te_3$ thin films**

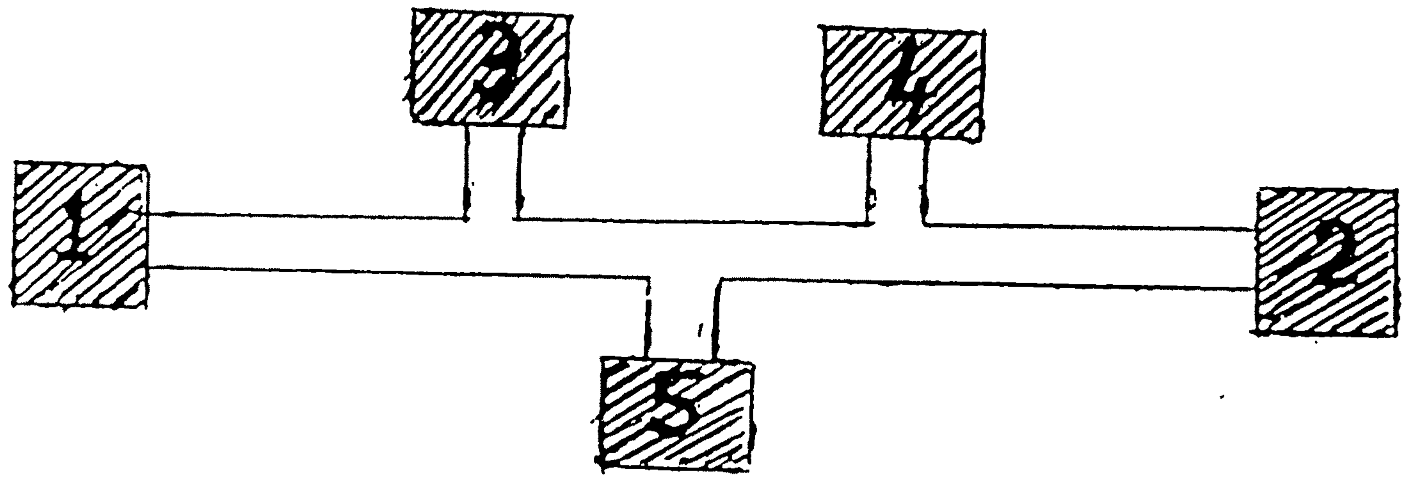

Figure - 10 : Goswami's linear probe geometry used for Hall measurement.

on to glass substrate through mica sheet masks appropriate for the bridge geometry.

The variation of carrier concentration and mobility of $In_xBi_{2-x}Te_3$, with x = 0.1, 0.5 films, deposited at two different substrate temperatures, with film thickness is shown in figures 11,12,13 and 14. It can be seen that in both the cases, the carrier concentration increases while the mobility decreases with increasing film thickness. Also the carrier concentration is larger whereas the mobility is smaller in the films deposited at higher substrate temperature.

The polarity of the Hall voltage indicated that $In_{0.1}Bi_{1.9}Te_3$ films are p-type in nature while that of $In_{0.5}Bi_{1.5}Te_3$, films were n-type in nature.

Metal Semiconductor Contact :

To evaluate the electrical properties of a semiconductor material an understanding of the type of contact made by different metals to the semiconductor and the effect of the contact on the measured property if any is necessary. When a metal semiconductor junction is formed, the type of contact obtained depends on the relative magnitude of work function of the metal (ϕ_m) and that of the semiconductor material (ϕ_s) as indicated below.

Nature of Contact	Ohmic	Rectifying
Metal-n-type semiconductor	$\phi_m < \phi_s$	$\phi_m > \phi_s$
Metal-p-type semiconductor	$\phi_m > \phi_s$	$\phi_m < \phi_s$

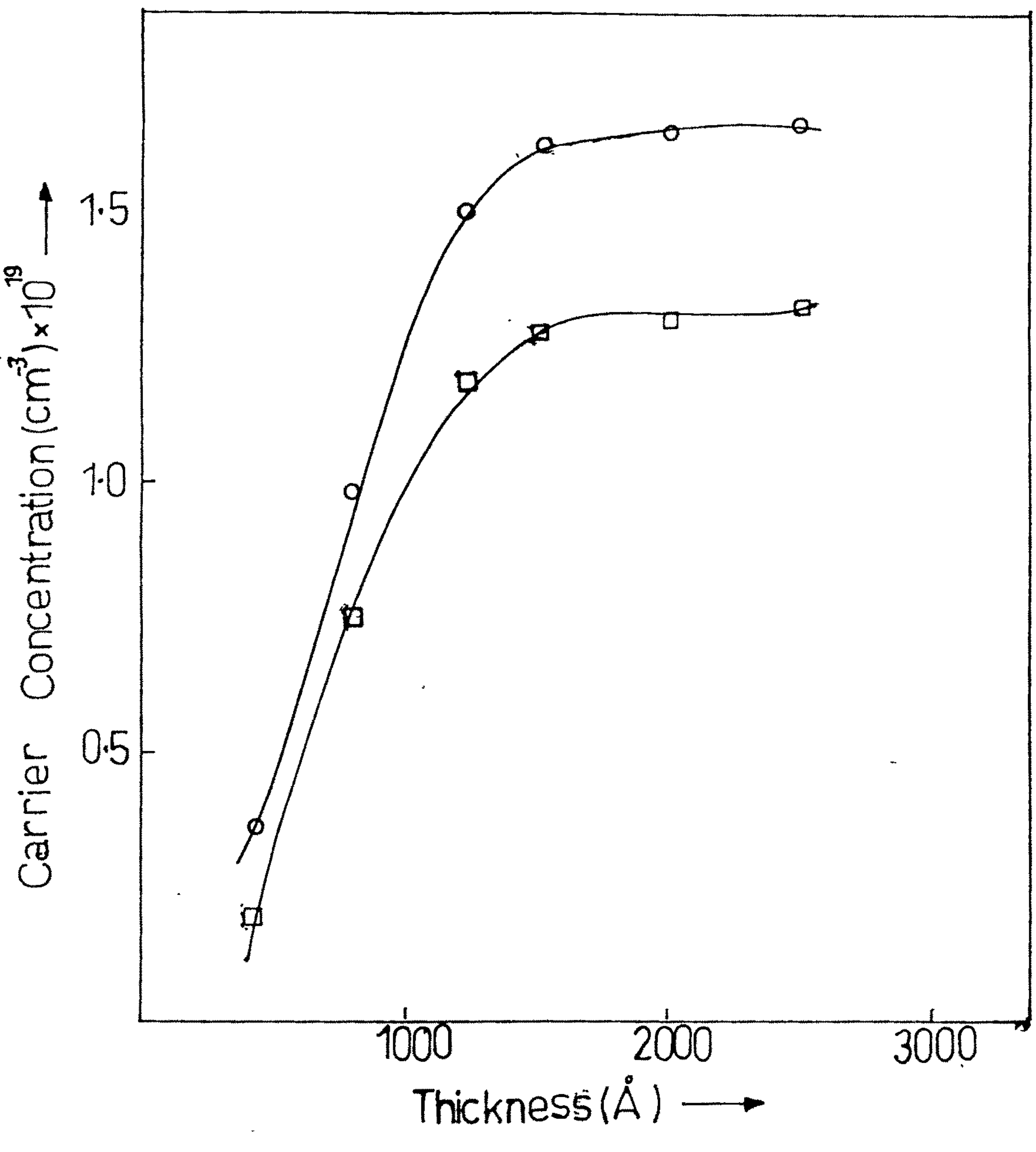

Fig.11 **Plots of carrier concentration (n) versus substrate temperature (T) for $In_{0.1}Bi_{1.9}Te_3$ thin films**

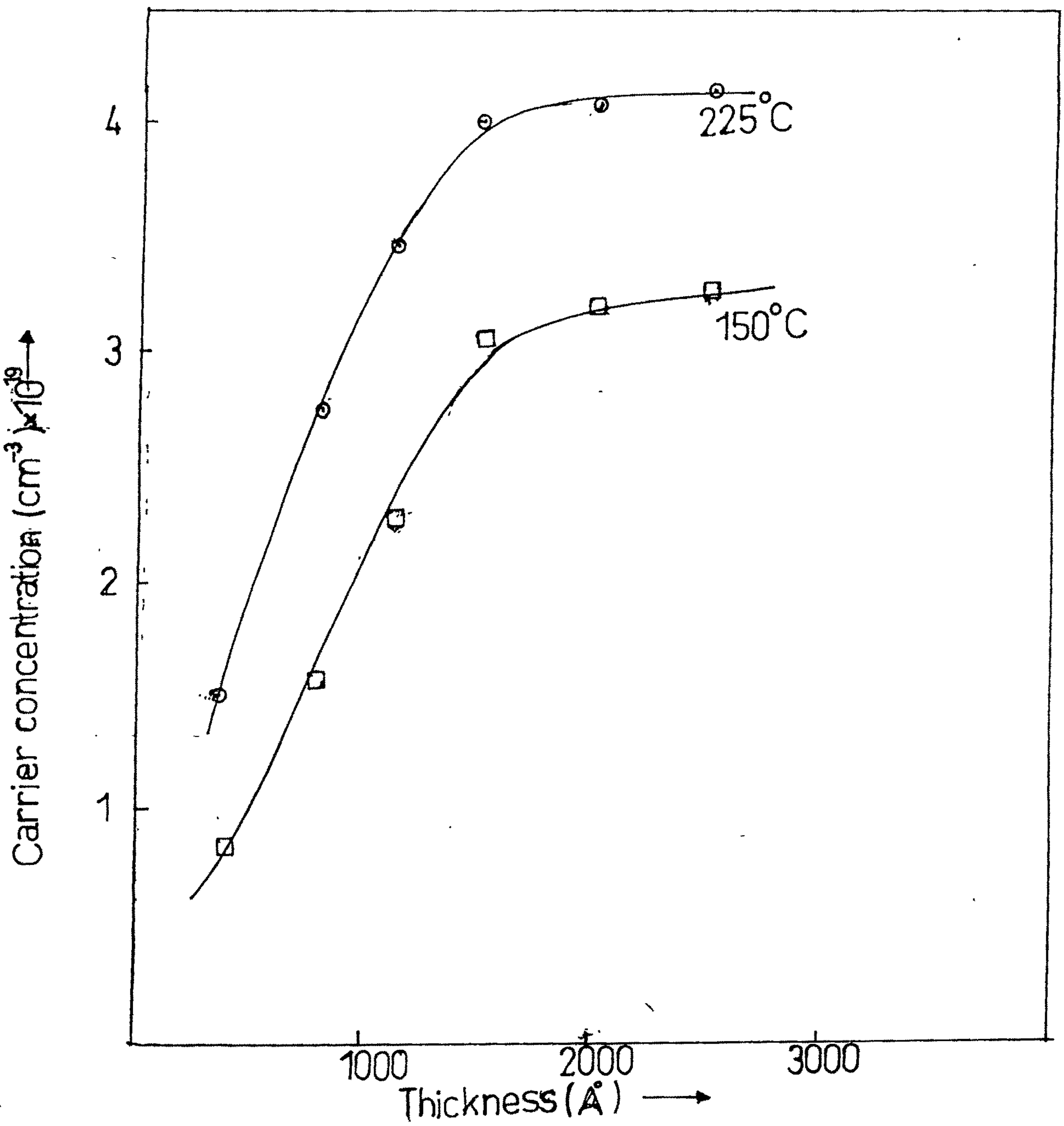

Fig.12 **Plots of carrier concentration (n) versus substrate temperature (T) for $In_{0.5}Bi_{1.5}Te_3$ thin films**

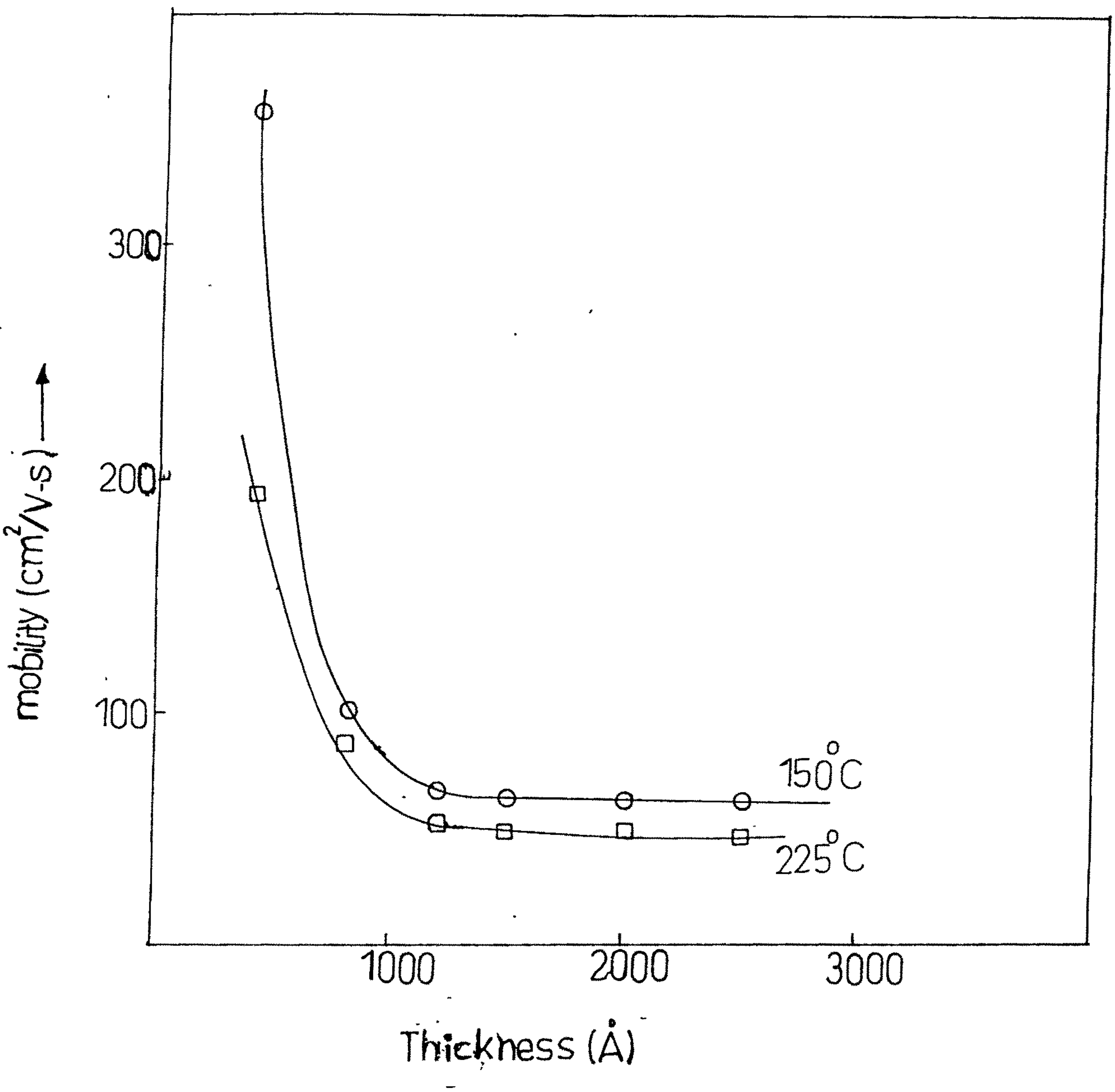

Fig.13 **Plots of carrier mobility (μ) versus substrate temperature (T) for $In_{0.1}Bi_{1.9}Te_3$ thin films**

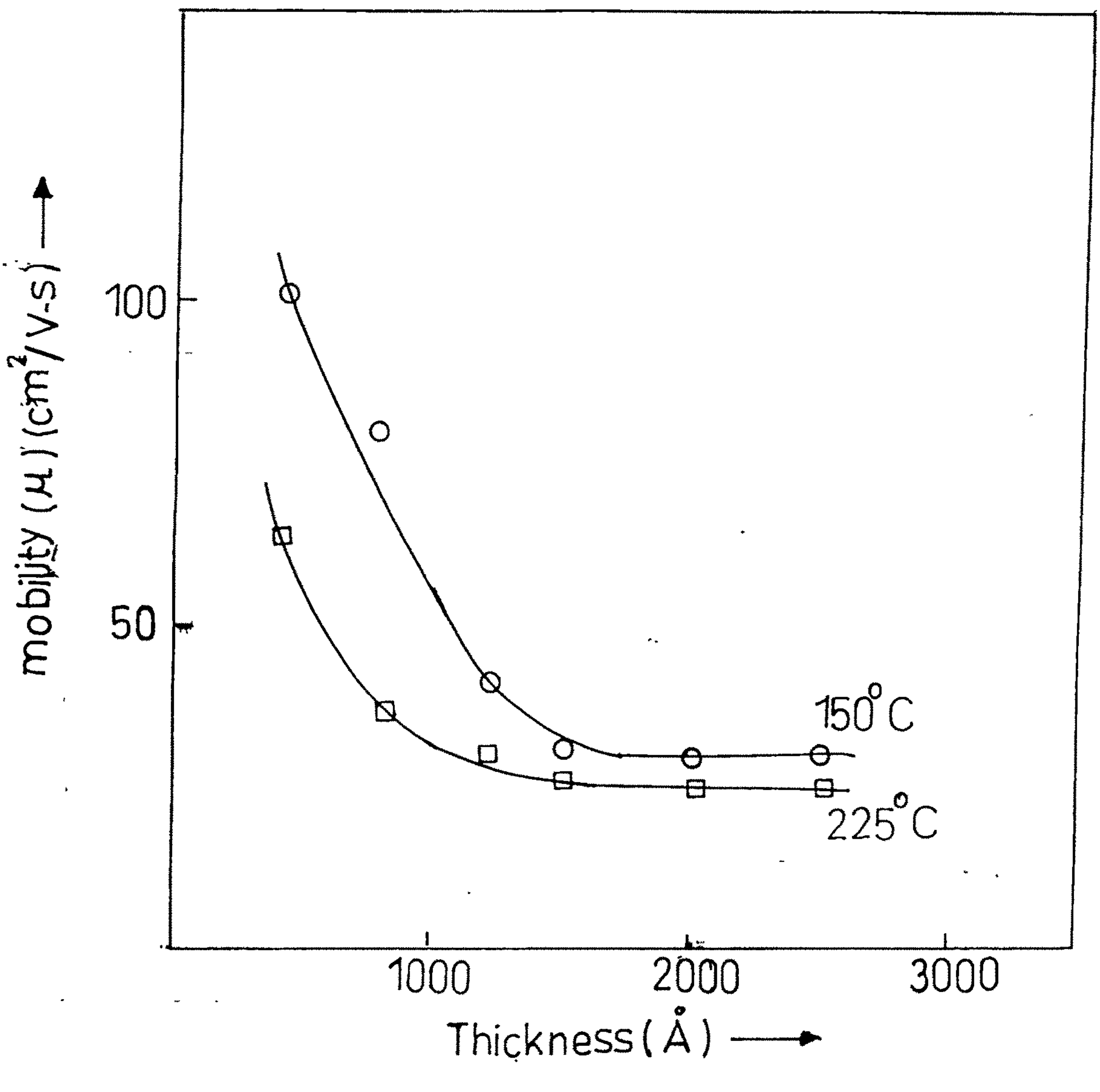

Fig.14 **Plots of carrier mobility (μ) versus substrate temperature (T) for $In_{0.5}Bi_{1.5}Te_3$ thin films**

Basically, an ohmic contact is a natural contact, which offers negligible resistance to the flow of current through the semoconductor for either polarity of bias voltage and is characterised by symmetrical I-V charactristics. A rectifying contact on other hand is a blocking contact, which offers some high resistance to the flow of carrent through the semiconductor for either positive or negative bias voltage and is characterised by non symmetrical I-V characteristics.

In the present study, three different contacts, viz., of Al, Sn and Ag films on the $In_{0.1}Bi_{1.9}Te_3$, films grown at 373K were studied using I-V characteristics.The metal contact of appropriate dimensions of 5x3 mm^2 and 500nm thickness were vacuum deposited side by side on $In_{0.1}Bi_{1.9}Te_3$ films using proper masking arrangement in order to make metal- semiconductor-metal structure. The I-V curves for different metal contacts on $In_{0.1}Bi_{1.9}Te_3$, film at room temperature are shown in Fig.15,16,17. The apparent resistance offered by these metal contacts increased in the following order: Al, Sn, Ag. It is observed that the Ag and Sn contacts exhibit good ohmic nature while Al contact exhibits good non-ohmic nature. Further, indium was also tried out. It was observed that indium diffuses into the $In_xBi_{2-x}Te_3$, film and results in an unstable and erratic nature of the device.

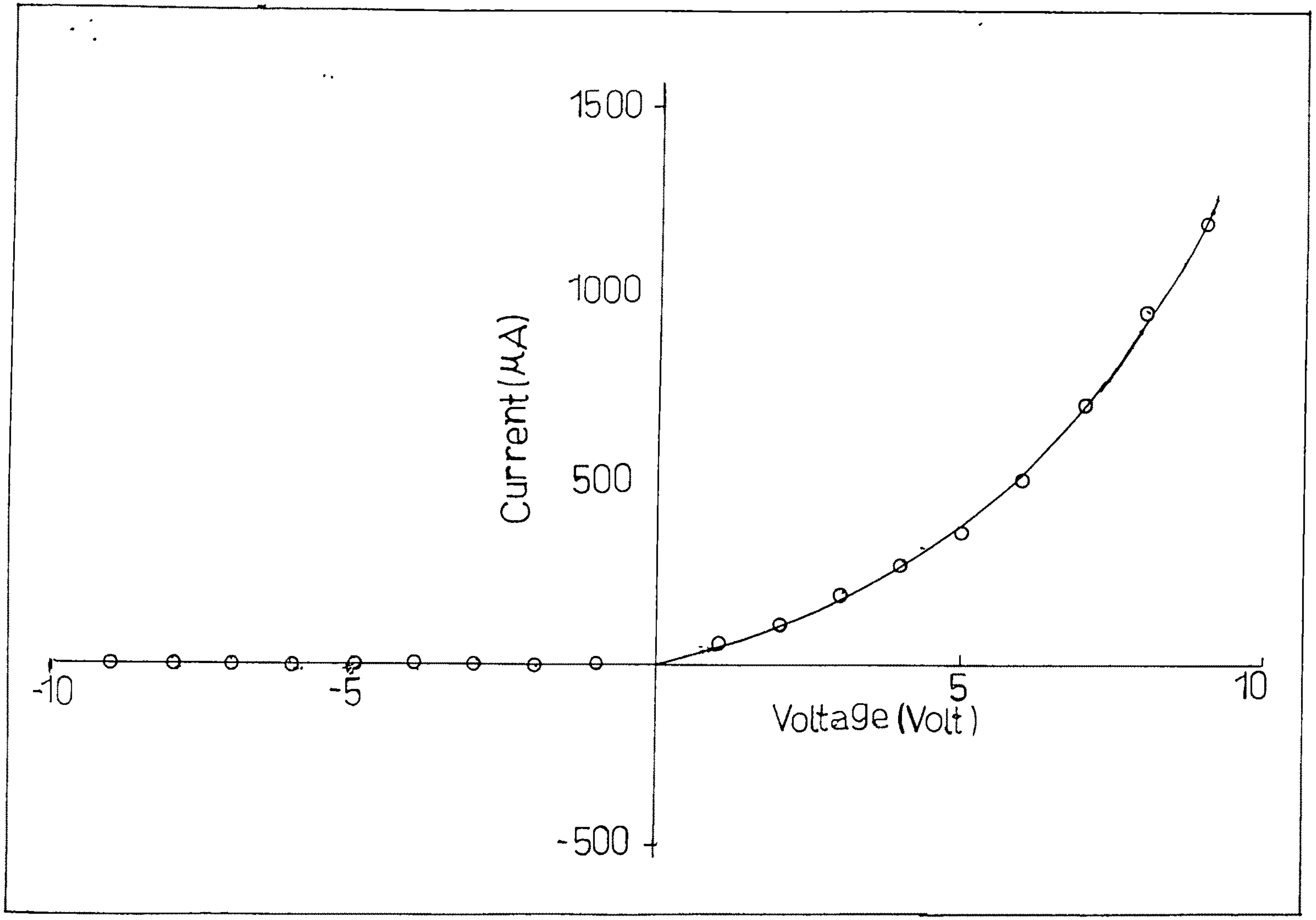

Fig.15 I-V charactristics for $Al/In_{0.1}Bi_{1.9}Te_3$, film at room temperature

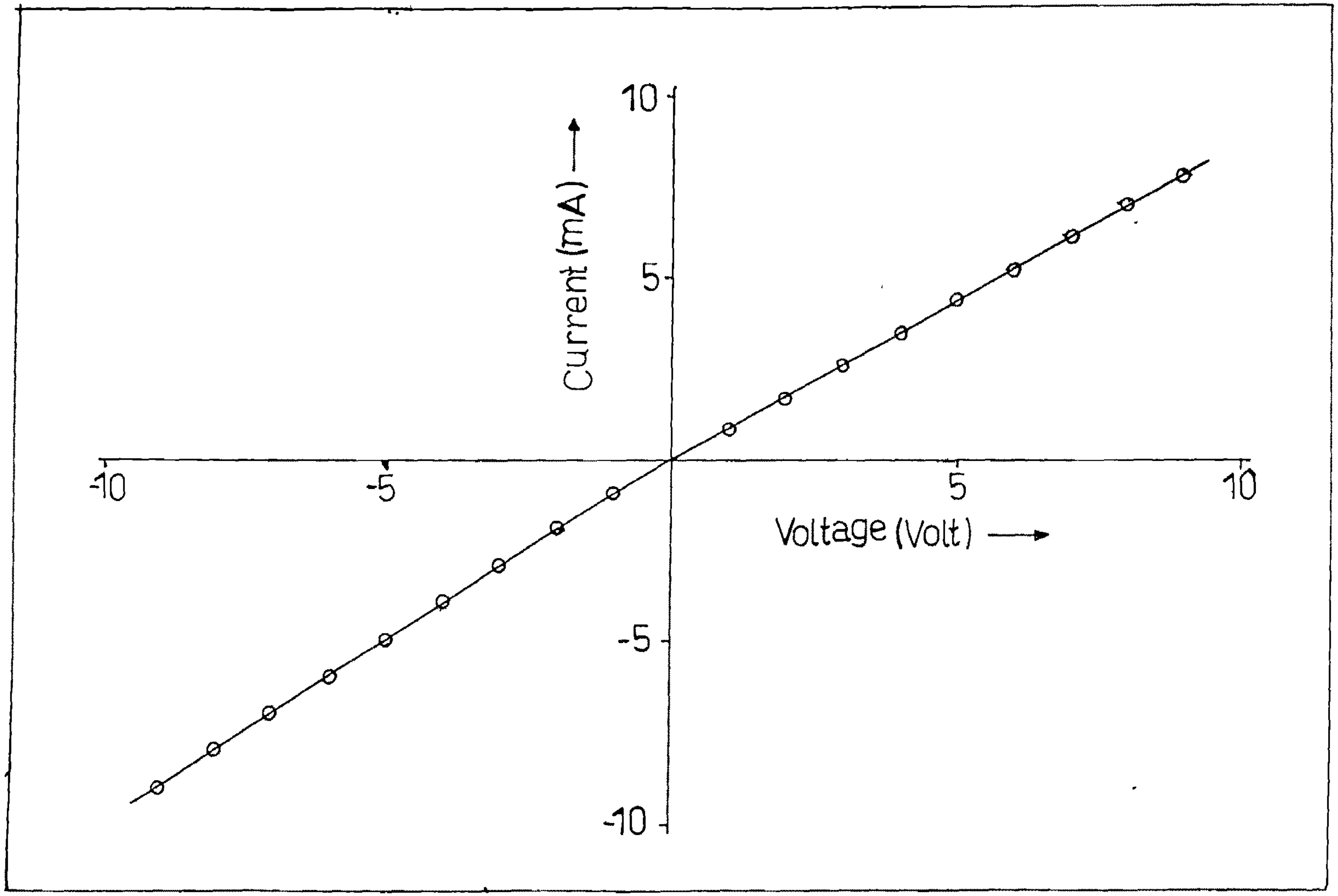

Fig.16 I-V charactristics for $Sn/In_{0.1}Bi_{1.9}Te_3$, film at room temperature

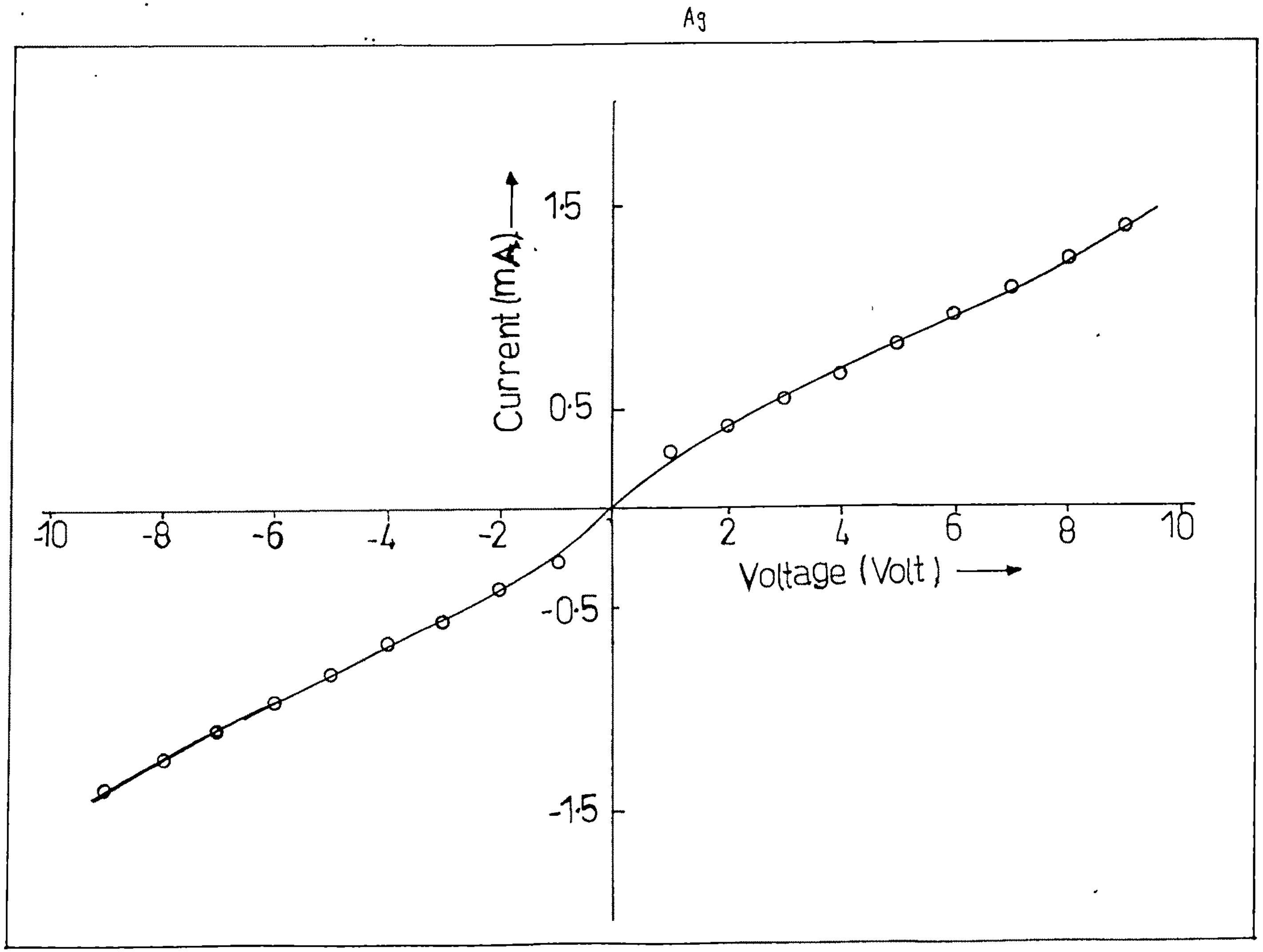

Fig.17 **I-V charactristics for $Ag/In_{0.1}Bi_{1.9}Te_3$, film at room temperature**

Schottky Diode Fabrication :

The $In_{0.1}Bi_{1.9}Te_3$, thin film of thickness about 130nm was deposited on the cleaned glass substrate by thermal evaporation technique. The substrate temperature for deposition of $In_{0.1}Bi_{1.9}Te_3$, film was kept at about 373 K. A residual pressure of the order of 10^{-5} Pa was maintained during the evaporation. The deposition rate was kept constant at about 0.5 – 0.8 nms^{-1}. The $In_{0.1}Bi_{1.9}Te_3$, films were annealed at 373K at 10^{-5} Pa for two hours in order to improve crystallinity as well as for stable electrical measurements. It has been observed, as described above, that Sn film shows good ohmic contact to the $In_{0.1}Bi_{1.9}Te_3$ film and can work as a back metal contact electrode, while Al film shows good non-ohmic contact to the $In_{0.1}Bi_{1.9}Te_3$, film.The area of diode was about 0.75 cm^2.

Fig.18 shows I-V characteristics of the Schootky diode. The forward bias corresponds to positive voltage applied to the Al electrode. The I-V curve shows good rectification with Al acting as a blocking contact [16]. Two of the most important parameters which play an important role in the device performance are the series resistance R_s and the shunt resistance R_{sh}. A convenient techniques to determine R_{sh} is to obtain it from the linear part of I-V characterisitc curve in the third quadrant, i.e., reverse bias. The series resistance R_s and shunt resistance R_{sh} are found to be 20 KΩ and 0.6MΩ respectively. The series resistance R_s is quite

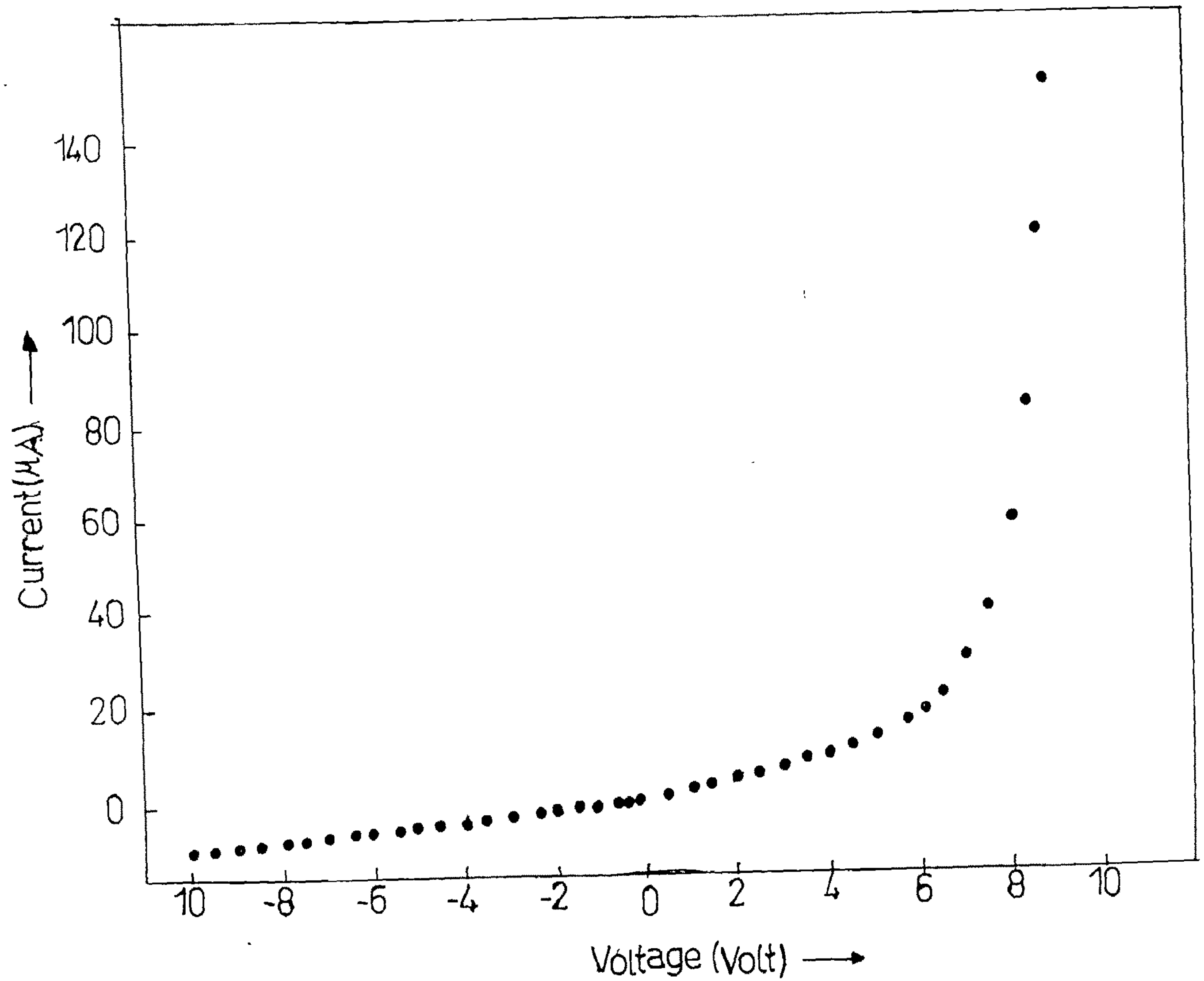

Fig 18 I-V characteristics of schottky diode

high compared to the values normally obtainable with metal-semiconductor junctions using wider band-gap semiconductors. The reason lies in the fact that in this narrow gap semiconductor the carrier concentration is quite high and in turn it has large resistivity. The junction formation is however satisfactory as implied by sufficiently large shunt resistance.

Fig.19 shows the plot of log I versus $V^{1/2}$. The linear nature of the plot indicates the dominant carrier transfer mechanism in this junction to be Schottky emission.

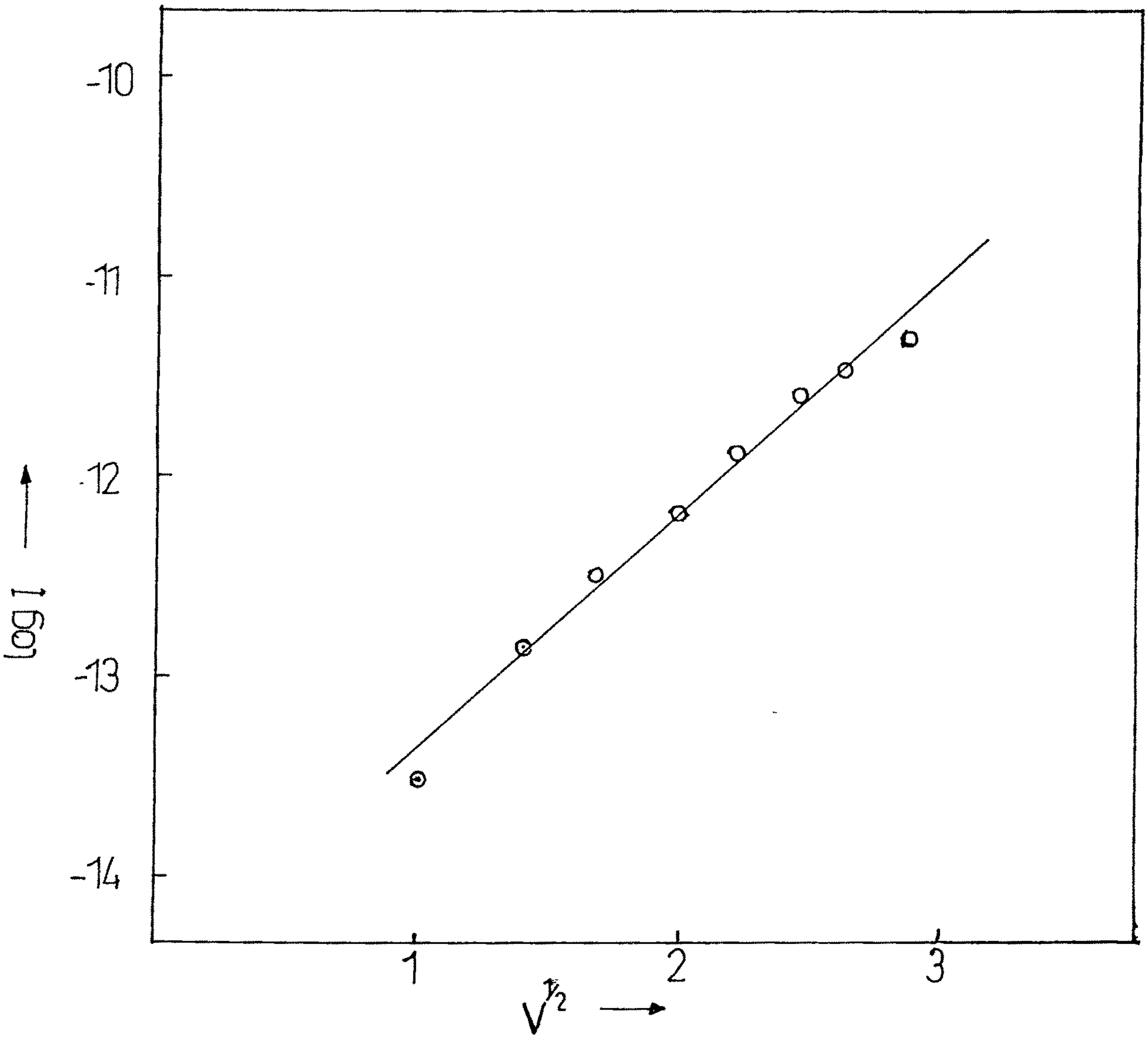

Fig.19 Plot of log I versus $V^{1/2}$

Conclusions :

1) The film thickness dependence of the band gap of $In_xBi_{2-x}Te_3$ with (x = 0.1 to 0.5) indicates the optical transitions to be governed by quantum size effect within the thickness range studied.

2) The variation of electrical resistivity, carrier mobility and carrier concentration of the $In_{0.1}Bi_{1.9}Te_3$, and $In_{0.5}Bi_{1.5}Te_3$, films with different thicknesses can be explained in terms of size effect and the variation with different substrate temperature can be explained on the basis of the stoichiometric composition and the variation in the crystallite size.

3) The metal semiconductor contact study reveals that Ag and Sn metals provide good ohmic contact, while Al provides non-ohmic contact to $In_{0.1}Bi_{1.9}Te_3$, film forming a Schottky barrier cell.

4) Hall measurement shows that $In_{0.1}Bi_{1.9}Te_3$, films are p – type while $In_{0.5}Bi_{1.5}Te_3$ films are n-type, the result reconfirming the p- to n- type transition observed in the case of the bulk crystals.

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