CHAPTER 4

CHARACTERISATION AND STUDIES OF THE VARIOUS PROPERTIES OF CVT GROWN $CuInS_2$ CRYSTALS

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4.1. INTRODUCTION

The ternary I-III-VI compounds have received much attention because, unlike their binary II-VI analogues, they can often be made usually both n- and p-type [1,2]. The largest-bandgap I-III-VI compound having this property is $CuInS_2$ (Eg = 1.5eV at room temperature) which has evoked technological interest both as an electroluminescent device [3] (note that the bandgap is close to that of GaAs), and as a photovoltaic device with a high theoretical solar cell efficiency [4].

For any type of device fabrication it is essential that the material is grown defect free in the form of single crystals and thin films and well characterised using different techniques before it is put to any technical use. Details of the chemical vapour transport crystal growth procedure and its use in the growth of single crystals of $CuInS_2$ has already been described in Chapter 3. A complete characterisation of these crystals with the available techniques has been carried out and the results thus obtained are described in this chapter.

4.2. EXPERIMENTAL

4.2.1. Determination Of Lattice Parameters

X-ray diffractograms of $CuInS_2$ samples were obtained with the help of X-ray diffractometer (chapter 2) employing CuK_{α} radiation. The diffraction pattern is shown in Fig.4.1.

The values of lattice parameters a and c obtained from the X-ray diffraction pattern are presented in **Table 4.1.** A comparison of these values with the data presented in chapter 1 clearly tells us that there is an excellent agreement of the lattice parameters with the reported values.

4.2.2. Composition

The composition of the grown crystals was studied with the help of Energy Dispersive Analysis of X-rays (EDAX) system attached with the Philips Transmission Microscope EM400 (chapter 2). The different parts of the single crystals of $CuInS_2$ were examined. The results of the analysis are shown in **Table 4.2.**

It is observed from the analysis given in the table that the crystals of $CuInS_2$ grown by the chemical vapour transport method possess more or less the stoichiometry composition of the elements. It is also confirmed from the EDAX analysis that except Cu, In and S no other impurity elements are present in the grown single crystals of $CuInS_2$.

4.2.3. DTA And TGA Analysis

Thermograms of $CuInS_2$ obtained in an open atmosphere are shown in Figs. 4.2 and 4.3. The specimen was in the form of powder for DTA and TGA measurements. The amount of specimen material for both the analysis was 10 mg. The thermogravimetric analysis combined with differential thermal analysis was carried out at a heating rate of $5^{o}C/min.$ upto $1000^{o}C$.

The DTA curve shown in Fig. 4.2 represents the percentage loss as a function of temperature. It is seen from this curve that a large exothermic peak occurs at $572.17^{o}C$. This is probably due to the volatility of excess sulphur reacting with oxygen forming sulphur dioxide. The loss of gaseous sulphur dioxide, is confirmed by weight loss observed at the same temperature in the thermogravimetric analysis graph shown in Fig.4.3.

A second endothermic peak observed at $746.43^{o}C$ in DTA graph was also observed by Binsma et al. [6]. They confirmed the existence of Cu and Cu_2S phase by using X-ray diffraction technique.

The phase transformation below $1000^{o}C$ as reported where $R_{\parallel}$ is resistance along the a-b plane

b is breadth

l is length

and t is the thickness of the specimen.

The results of the resistivity measurements are given in **Table 4.3.** The variation of resistivity with temperature is shown in Fig. 4.4. A careful study of **Table 4.3** and Fig. 4.4. reveals the following points.

1. In the case of all $CuInS_2$ samples, the resistivity goes on decreasing with the increase in temperature, thereby confirming their semiconducting behaviour.

2. The activation energy obtained from the plot of log $\rho_{\parallel}$ vs 1/T comes out to be 0.13eV.

4.2.5. Semiconducting Nature Of The Grown Crystals

Hall measurements, Seebeck coefficient measurements etc. could not be carried out on the as-grown samples of $CuInS_2$ crystals because of the high values of room temperature resistivity possessed by them. The semiconducting nature of the grown crystals was therefore investigated by the hot probe method described below.

It is well known that if a metallic specimen is connected at its two ends with a second metal, and if one of the junctions is heated, a voltage is developed across the open ends of the second metal. A schematic circuit diagram for the measurement of thermoelectric voltage for a semiconductor is shown in Fig.4.5.

If metal contacts are applied to the two ends of a semiconductor rod and if one of the junction is maintained at a higher temperature, a potential difference is developed between the two electrodes. This thermoelectric voltage is produced partly because

(1) The majority carriers in the semiconductor diffuse from the hot to the cold junction, thus giving rise to a potential difference between the two ends of the specimen. This voltage builds up to a value such that the return current, just balances the diffusion current when a steady state is reached.

(2) Other part which contributes to the thermoelectric voltage is the contact potential difference between the metal and semiconductor which occurs at the two junctions.

In the case of $CuInS_2$ single crystals, since the contacts occuring at the two junctions are ohmic in nature, the voltage due to second part is negligible. Therefore, the potential obtained due to the temperature gradient across the semiconductor is only due to the first part. The type of conductivity can be determined from the sign of the thermoelectric voltage by employing the method given below.

When the probe connected to the positive terminal of the voltmeter is heated and connected to the semiconductor, then if the charge carriers are predominantly electrons they will flow towards the negative terminal making it more negative and positive voltage will be observed on the voltmeter. This will indicate that the specimen exhibits n-type conductivity and is therefore an n-type semiconductor.

Similarly when the probe connected to the negative terminal of the voltmeter is heated and connected to the semiconductor, then if the charge carriers are predominantly electrons, they will flow towards the positive terminal making it less positive and a negative voltage will be registered on the voltmeter. This will indicate that the specimen exhibits n-type conductivity and is therefore an n-type semiconductor.

Using the technique described above it was seen that $CuInS_2$ single crystals grown in the present investigation are n-type semiconductors.

4.2.6. Optical Band Gap Measurements

A study of the interband absorption near the threshold of its rapid increase (near the absorption edge) can obviously provide information on the structure of the electron energy spectrum near the top edge of the valence band and the bottom edge of the conduction band. This information is of essential importance for the determination of the semiconductor properties. Therefore, the measurement of the absorption coefficient constitutes the most important means of determining the band structure of semiconductors.

The optical absorption spectra on $CuInS_2$ single crystal samples was obtained on UV-VIS-NIR Shimadzu spectrophotometer (chapter 2) in the range 400 nm to 900 nm. The absorption data was analysed in terms of the theory of Bardeen et al. [8], which gives for a direct transition.

$$\alpha = \beta\ (h\nu - E_g)^r / h\nu$$

where β is a constant, E_g is the optical bandgap and h is the energy of the incident photon, r assumes values

2 and 1/2 for allowed direct and indirect transitions respectively.

It is observed that for $CuInS_2$ single crystal, the absorption can be explained satisfactorily with r=2 in the energy range 400 nm to 900 nm. A plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 4.6. The intercept obtained by extrapolation of the linear portion of the plot on the energy axis gives a bandgap value of 1.53 eV. From the functional dependence obtained for the absorption coefficient on photon energy, it may be seen that the transition is a direct allowed one. This value of E_g compares favourably well with the values reported in the literature [9,10].

4.3. DISCUSSION

Since chalcopyrite $CuInS_2$ single crystal growth by melt is hindered due to two solid state phase transitions, CVT technique was found to be more appropriate for its growth. Successful growth of $CuInS_2$ single crystals was therefore carried out by employing a CVT technique using iodine as the transporting agent. The as-grown $CuInS_2$ crystals were structurally characterised by X-ray diffraction technique. The lattice parameters obtained from these studies were found to be in good agreement with the reported values. The crystals were all found to be nearly stoichiometric as evidenced by EDAX analysis.

The thermal analysis of as-grown $CuInS_2$ showed an additional exothermic peak at 572.17^{o}C in the DTA curve other than the regular endothermic peak at 746.43^{o}C observed by earlier investigators [6,7]. This additional exothemic peak in DTA at 572.17^{o}C in the present case could be due to heating carried out in an open atmosphere in contrast to reported analysis by earlier workers which was performed is an inert atmosphere. Open atmosphere heating could give rise to formation of sulphur dioxide due to reaction of excess volatile sulphur with atmospheric oxygen. The weight loss observed at nearly the same temperature range in the TG graph, confirms this formation of sulphur dioxide. The second endothermic peak at 746.43^{o}C is synonymous with the earlier reported work. The 980^{o}C peak observed by Binsma et al. [6] could not be traced in the present investigation. This could be due to its shifting above 1000^{o}C because of the analysis being performed in an open atmosphere.

The room temperature resistivity value of the as-grown single crystals was found to be in the range of 10^5-10^6

ohm cm. The high resistivity of these crystals indicates that the crystals are more stoichiometrically perfect. This observation is in agreement with the stoichiometric analysis carried out by EDAX.

The low value of activation energy obtained from Fig.4.4 in the temperature range 303K to 383K indicates the presence of extrinsic i.e. impurity conduction in the observed range of temperature. Due to experimental limitation, electrical resistivity variation could not be studied at still higher temperature range.

The measurements carried out by the hot probe technique showed that the crystals of $CuInS_2$ were n-type.

The direct character of the band gap is a common property of the ternary I-III-VI_2 chalcopyrite compounds [8,9] and has been confirmed by band structure calculations for $CuInS_2$ [11]. The optical absorption measurements carried out on these crystals clearly indicate that they show a direct transition across the energy gap. The value of E_g is in good agreement with the reported values.

4.4. CONCLUSIONS

1. Single crystals of $CuInS_2$ of quite large size have been

grown by using chemical vapour transport technique with iodine as the chemical transporting agent.

2. The X-ray diffraction studies of the crystals indicate that they are single phase $CuInS_2$ with crystallographic lattice parameters in complete harmony with the reported values. The crystals were found to be nearly stoichiometrically perfect by EDAX analysis.
3. Thermal analysis of $CuInS_2$ compound in atmosphere showed the presence of an exothermic peak at 570^{o}C, which was ably supported by the observation of weight loss in TGA at this temperature. The second additional peak at 746^{o}C has been attributed to formation of Cu and Cu_2S phase.
4. The as-grown crystals showed room temperature resistivity in the range of 10^5-10^6 ohm cm and were found to exhibit n-type semiconducting behaviour.
5. From the absorption analysis, the transition energy between the valence and conduction band has been identified as a direct transition with a bandgap of 1.53eV.

TABLE 4.1 Lattice parameters of $CuInS_2$ single crystals

Parameters	Observed	Reported	Reference
a	5.505 A°	5.52 A°	[5]
c	11.324 A°	11.12 A°	[5]

TABLE 4.2 Wt % observed by EDAX analysis

Different Elements	Observed wt. %	Standard Wt. %
Cu	26.176	26.203
In	48.869	47.350
S	24.955	26.447

TABLE 4.3 High Temperature (R.T. to 383 K)
Resistivity Data Of n-$CuInS_2$

Temperature ^{o}K	Resistivity value ohm. cm.
295	4.36×10^5
303	3.82×10^5
313	3.39×10^5
323	2.87×10^5
333	2.59×10^5
343	2.31×10^5
353	2.16×10^5
363	1.82×10^5
373	1.57×10^5
383	1.31×10^5

CAPTIONS TO THE FIGURES

Fig.4.1. X-ray diffractometer trace of $CuInS_2$.

Fig.4.2. DTA curve for $CuInS_2$.

Fig.4.3. TGA curve for $CuInS_2$.

Fig.4.4. Variation of electrical resistivity with temperature.

Fig.4.5. Schematic circuit diagram for the measurement of thermoelectric voltages.

Fig.4.6. Optical absorption $(\alpha h\nu)^2$ as a function of photon energy $h\nu$.

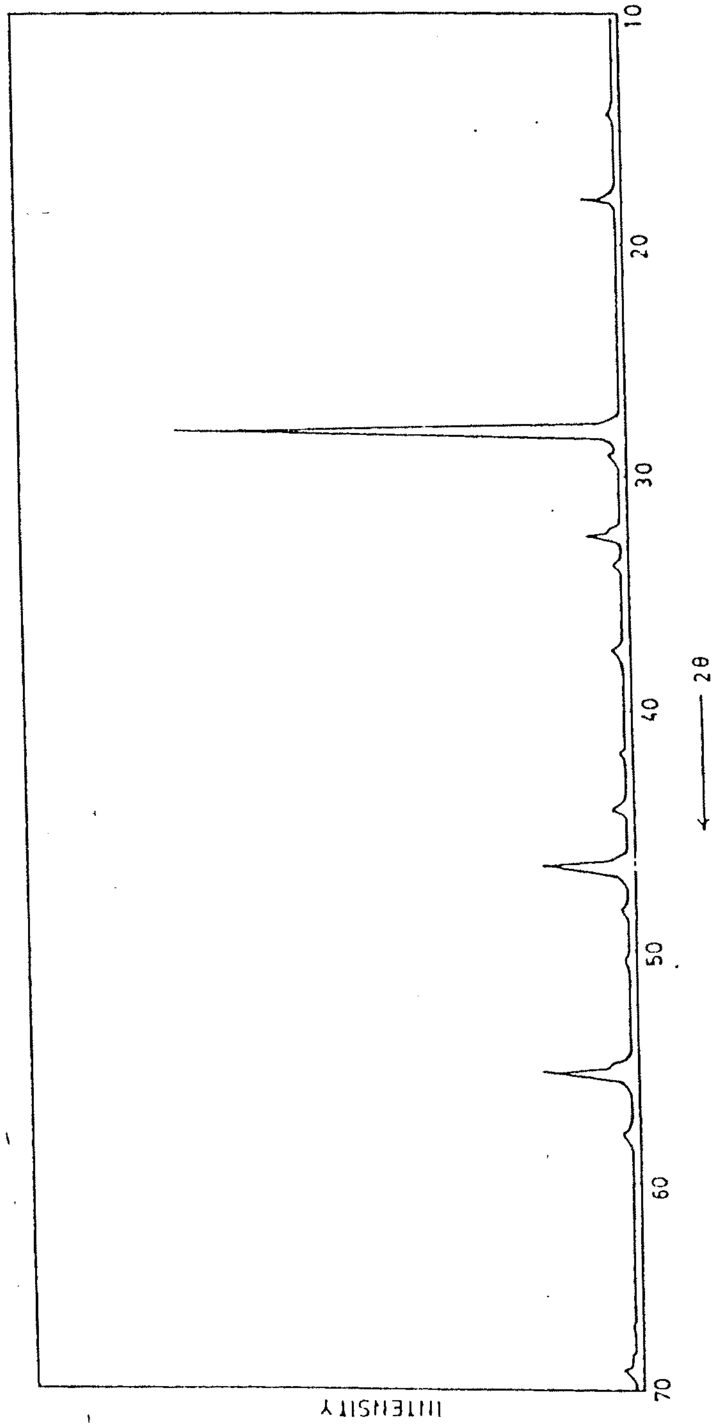


Fig. 4.1

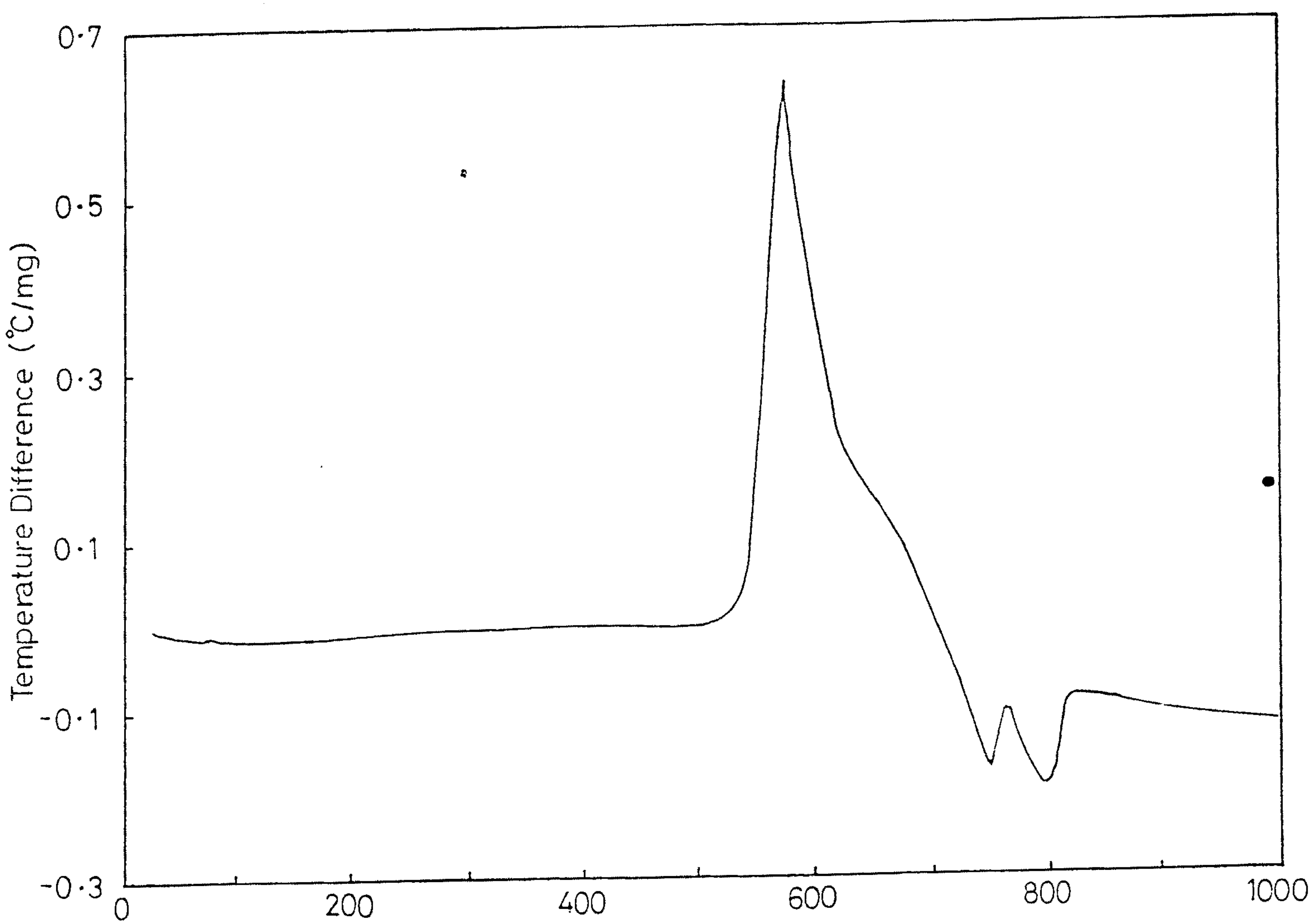

0·7
0·5
0·3
0·1
-0·1
-0·3
Temperature Difference (°C/mg)
0
200
400
600
800
1000
Temperature (°C)

Fig. 4.2

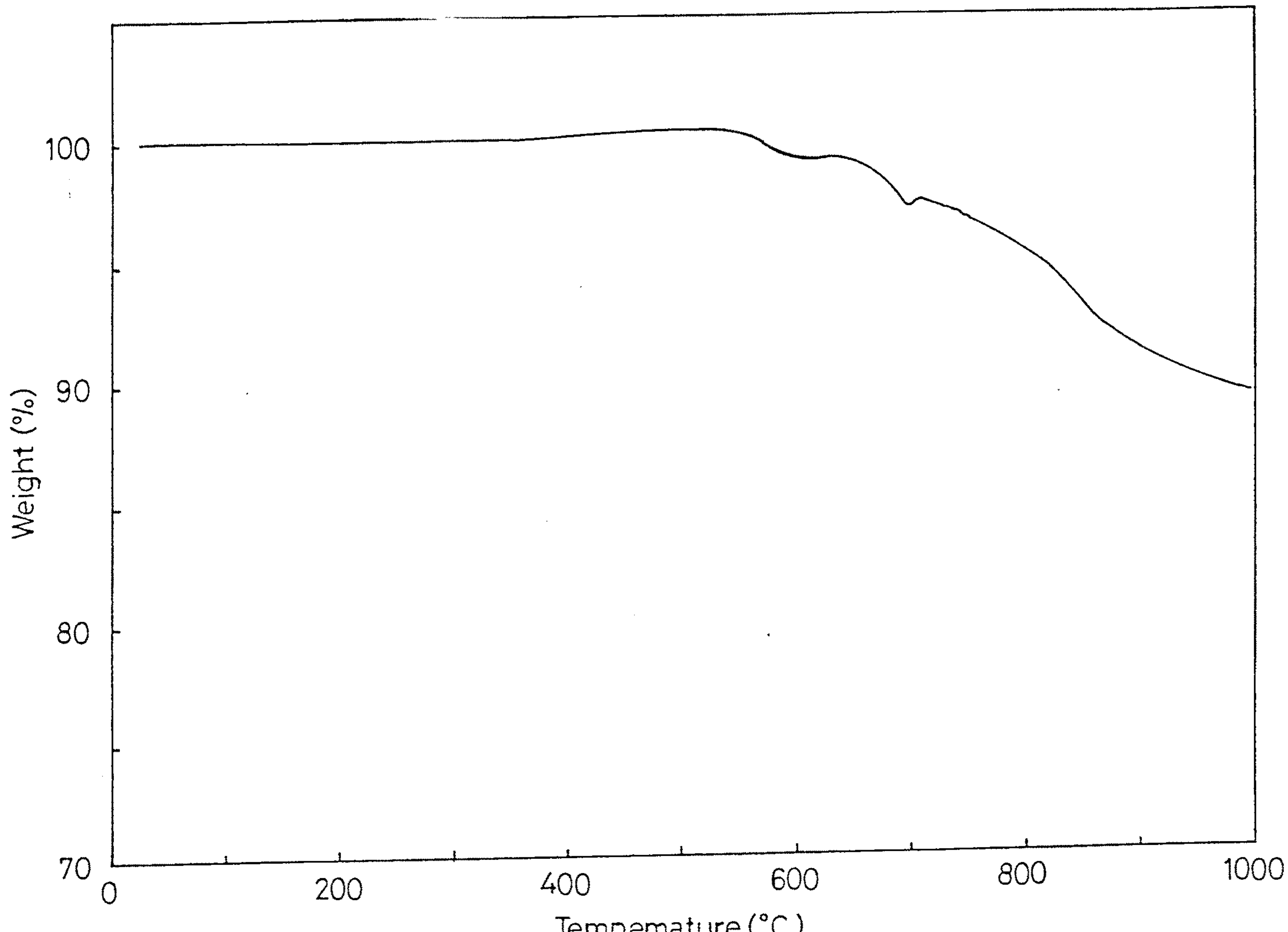


Fig. 4.3

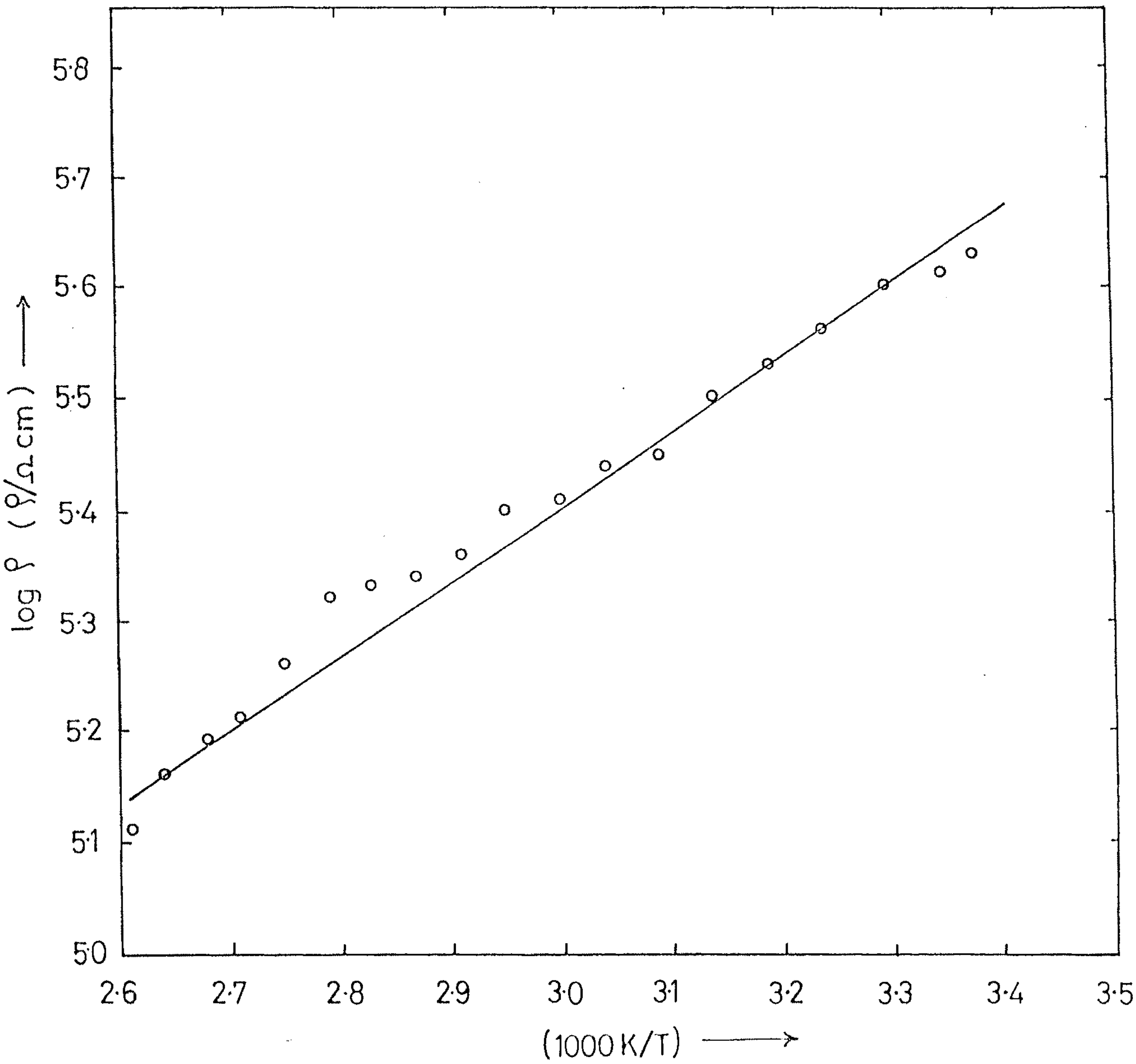
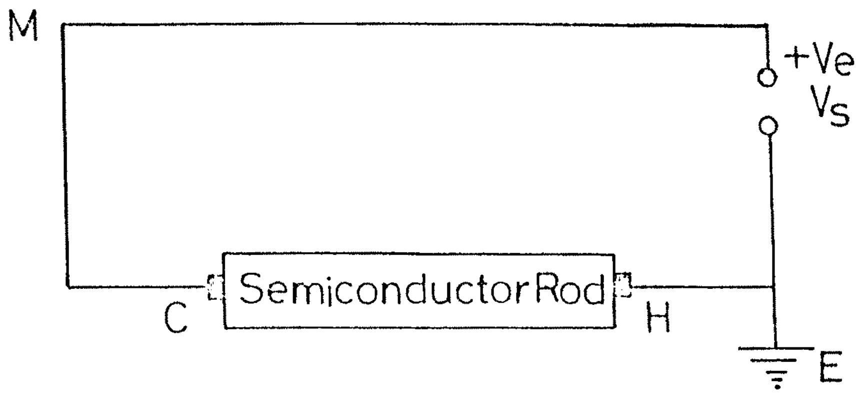

5·8
5·7
5·6
5·5
5·4
5·3
5·2
5·1
5·0
log ρ (ρ/Ω cm) ⟶
2·6
2·7
2·8
2·9
3·0
3·1
3·2
3·3
3·4
3·5
(1000 K/T) ⟶

Fig. 4·4



M Metal Conductor

C Cold Junction

H Hot Junction

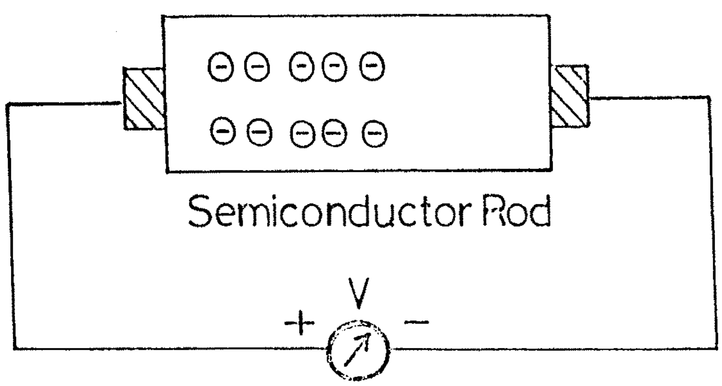


Fig. 4.5

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