CHAPTER 3

RESULTS AND DISCUSSION

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The electrical transport properties of amorphous semiconducting Se-Te-In system, are discussed here. Amorphous structure of the material, under study is confirmed from the X-ray diffraction pattern, which consist of broad rings, vanishing rapidly with increasing angle, without any evidence of spots or sharp rings.

Before experimental work, all samples Se_{70} - Te_{30}, Se_{70} - Te_{30-x} - In_x (where x = 1,3,5,7,9% atomic weight) are heated in an electric furnace up to 110°C, and the temperature (110°C) is kept constant for half an hour. For the study of I-V characteristics, electrical conductivity, thermopower and magnetic susceptibility, the annealed smaples are used. The effect of annealing on amorphous structure is that, the probability of heteronuclear bond formation is more than the homonuclear bonds. So, more ordered structure is formed, which causes decrease in band gap of the material, and altimately increase in conductivity [1].

Current voltage characteristics at different compositions are shown in Fig. (2.11). The I-V curves are symmetric in nature. For each sample breakdown occurs at certain voltage. Break-down voltage increases with increase in

Indium concentration, (break-down voltage range 70-170volt). Ovshinsky reported the discovery of non-destructive fast electrical switching in thin films of multicomponent chalcogenide glasses. It is found that, because of annealing, conductivity of the samples is increased to greater extent. For small voltage, across the samples (pellet), current in (mA) is observed.

When a certain critical voltage is reached, the material is converted in to a highly conductive state. When the voltage is decreased, the material revert back to its original state. This type of behaviour is observed for all samples. Whether the switching is either of thermal or of purely electronic nature is a problem of discussion. Switching mechanism is discussed in Chapter I.

Here we would like to discuss the non-linear I-V behaviour on the basis of charge-defect, states, introduced by Kastner and Hudgens [2]. They proposed that in amorphous semiconductors the lower energy defect states are positively charged three-fold coordinate C_3^+ and negatively charged, one-fold coordinate C_1^- chalcogen atoms. When an electric field is applied to an amorphous semiconductor, electrons and holes and injected from the cathode and anode in to the material. Initially the injected electrons and holes are held up at the electrodes, as there is no internal electric field. At the electrode the electrons are traped by C_3^+ (donors) centres, which transform to C_3° neutral centres. At the cathode the C_1^- centres capture the holes and transform to C_3° neutral centres. The electrons are captured at faster rate than the holes, because, the mobility of electrons is higher than that of holes. This will result in creating a higher concentration of C_1^- centres as compared to that of C_3^+ centres. Thus at the anode a high field exists, and holes drift towards the cathode, where they are captured by the C_3° neutral centres, thus creating C_3° centres at the cathode. This increases the field at the cathod and thus electrons drift from the cathode towards the anode, where they are again captured by the C_3° centres, and C_1^- are formed.

The experimental conductivity data of five samples of the system Se_{70}-Te_{30-x} -In_x (where x=1,3,5,7% atomic weight) is listed in table 3.1. The conductivity is represented by Mott's equation

$$\sigma = C \exp.\left(\frac{E\sigma^*}{kT}\right) \qquad ..(3.1)$$

The values of activation energies E_σ^* obtained from the curves drawn between logσ against 1/T and the preexponential factor C, are listed in table 3.1. It is observed that, conductivity decreases with increase of Indium concentration in the samples. For Se_{70}-Te_{30}, activation energy is 0.35eV and increases to 0.43 electron volt for Se_{70} - Te_{23} In_7 . It is suggested by Haisty and Krab [3] that the incorporation of Sb in Se-Te is regarded as forming mixed rings and strong covalent bonds, between the atoms in the rings. The addition of Sb leads to cross-linking between the chains promoting the formation of three dimensional network. The addition of Sb weakens the bonds in rings which will influence the band structure of the material and hence electrical properties. We may think on the same line fcr our system Se-Te in which Indium is incorporated. One may expect that, similar to the system Se-Te-Sb, we must get increase in conductivity with increase in In concentration. Such type of behaviour is not observed for our system. It is found that, with increase in In concentration, the conductivity decreases. This contradiciton may be due to, annealing of samples (up to 110°C).

Due to annealing, oxide layers may be formed, in the bulk of the material. Since the conductivity decreases with increasing Indium concentration, the formation of Indium oxide layers in the bulk, is more probable, which altimately cause decrease in conductivity. Conductivity measurement, before and after polishing the surfaces of sample, confirms that, the oxide layer is not formed at the interface between electrode and sample.

Fig. (2.14) shows variation of room temperature conductivity, with indium concentration. It is seen from figure that, conductivity decreases with increasing Indium concentration.

Fig. (2.15) shows variation of pre-exponential factor 'C' against concentration of Indium. From this curve we find that the pre-exponential factor 'C' is not constant but depends up on glass composition. The value of 'C' lies between 0.81×10^{-3} to $0.26 \times 10^{-3} \Omega^{-1} cm^{-1}$; for different concentrations of Indium in Se-Te. Mott and Davis [4] argued that, there is no definite correlation between the intercept 'C' and activation energy E_6^* of amorphous semiconductors. However the present investigations show that 'C' increases with decrease in activation energy. According to Mott and Davis the intercept 'C' is related to density of localized state. As 'C' increases the density of localized states decreases. Thus observed increase in 'C' with composition probably suggest the formation of glass composition with higher degree of disorder. This behaviour is also explained by Majid et.al. [5].

Fig. (2.16) shows variation of room temperature conductivity with activation energy. It has been observed that the conductivity increases with decrease in activation energy, which is in agreement with observations given by Majid [5], for the system $(As_2 - Se)_{1-x}(Tl_2 Se_3)_x$. The variation of E_6^* with concentration x and E_6^* with 'C' is shown in Figs. (2.17, 2.18). Figure (2.17) shows that as Indium concentration increases in the sample, the activation energy increases. It means, the conductivity of the sample decreases as the Indium concentration increases.

Figs. (2.27 - 2.31) shows variation of conductivity with field strength, at different temperatures. It is observed that, the conductivity increases with increase in field strength, at room temperature. This increase in conductivity at room temperature is found to depend, on Indium concentration in Se-Te system. As Indium concentration is increased, less increase in conductivity is found. It is found that, above 60°C, the conductivity becomes independent of field strength.

At room temperature the charge carriers are accelerated, due to applied field. As field is increased, more and more charges reach to anode, resulting increase in current. At high temperature the number of charge carriers are more as compared to room temperature, but the effect of field is not predominent.

Fig. (2.20) shows variation of thermo e.m.f. with temperature difference. It shows that the thermo e.m.f. varies linearly with temparature difference. As we get positive thermo e.m.f. for the sample, the charge carriers are holes, and the material is p-type in nature. The variation of thermoelectric power with 1/T°K is shown in Fig. (2.21). It is observed that the thermoelectric power varies linearly in all the samples. There is increase in thermoelectric power with increase in Indium in Se-Te.

The thermoelectric power equation given by Fritzsche [6].,

$$S = \frac{k}{e} \left(\frac{E_s^*}{kT} + A \right) \qquad ..(3.2)$$

is used to calculate the activation energy. For most of the chalcogenide glasses A =1. The activation energy calculated from the curves comes out to be 0.23 eV for Se_{70}- Te_{30} and increases to 0.35 eV for Se_{70}- $Te_{30}In_7$.

The activation energy increases as the percentage of Indium in Se-Te system increases. The difference in activation energy, calculated from the conductivity and thermoelectric power measurement is, $(E_Q = E_\sigma^* - E_s^*) \sim 0.1$ eV. The values of E_s^* and E_Q are listed in table no. 3.1. Several models have been proposed to explain the features found experimentally for the difference in activation energy, calculated from conductivity and thermoelectric power. For chalcogenide P. Nagels [7] proposed ambipolar transport. This difference in activation energy (E_Q), could represent an activation energy in the mobility, $\mu(T)$, which enters the expression for σ i.e.

$$\sigma = \int_{-\infty}^{\infty} g(E) f(E) e \mu(E) dE, \qquad ..(3.3)$$

but not for S. In that case, conduction could be due to small-polaron hopping. However the conductivity data appear to require sufficiently large mobilities, that this mechanism is highly unlikely [8]. At the present time, none of the three standard transport properties σ, S and R_H can be considered to be understood. It is clear that σ can be modulated over many orders of magnitude both by n-type and p-type doping. Overhof and Beyer [9] have reported difference between activation energies as 0.1 to 0.2 eV for chalcogenide glasses, and a Si:H. They have also discussed various transport modes considering the transport properties of both chalcogenide and a Si:H, simultaneously. They have defined Q(T) by the following relation,

$$Q\,(T) = \ln\,(\sigma(T)\,\Omega^{-1}\mathrm{cm}^{-1}) + \frac{q}{k}\,S(T) \qquad ..(3.4)$$

With $q=-|e|$ for electrons and $q=+|e|$ for holes. They have also shown that both for silicon and chalcogenide the Q(T) curves are generally well represented by,

$$Q(T) = Q_O - \frac{E}{k\,T} \qquad ..(3.5)$$

Following Overhof and Bayer, we have plotted the graph of Q(T) against T^{-1} k for our system as shown in Fig.(2.23). The slope of curve yields Qo values which are presented in table (3.1). Many attempts have been made to explain the non-zero value of E_Q,[9]. When transport takes place in the extended states, above the mobility edge,

$$Q(T) = \ln\,(\,\sigma_{min}\,\Omega^{-1}\mathrm{cm}^{-1}\,) + 1 \qquad ..(3.6)$$

The values of E_Q obtained from above equation are in agreement with values reported in the literature [10]. The non-zero slope of Q(T) is due to long range static potential that modulates the energy of mobility edge in space [9]. The origin of this potential could be electrostatic potential of charged centres which are probably not homogeneously distributed in space than rondom distribution. In this case variation of E_Q with preparation and doping level had to be attributed to long range potential. It has been reported that, in highly doped or more disordered samples E_Q may as large as 0.25 eV, while for undoped sample $E_Q = 0.05$ eV [11].

The plot of $\ln\sigma$ against S is shown in Fig. (2.22). The slope of which enables to calculate σ_0 . It seems to us that further work both theoretical and experimental is necessary to determine σ_0.

The conductivity is given by,

$$\sigma = \sigma_0 \exp. \left[- \frac{E_c - E_F}{kT} \right] \qquad ..(3.7)$$

at zero temperature

$$\sigma_0 = \frac{0.03\ e^2}{h\ l_1}$$

where l_1 is inelastic diffusion length, σ_0 is obtained from the slope of $\ln\sigma$ against S curves the values of l_1 are listed in table 3.1.

Magnetic susceptibility measurements shows that, the sample is diamagnetic in nature. The diamagnetism is found to depend on Indium concentration in the Se-Te system. It is found that diamagnetism decreases with increase in Indium concentration. This may be due to the dependence of diamagnetic susceptibility on Z, (atomic number). The dependence of magnetic susceptibility on temperature Fig. (2.26) shows that χ(T) nearly remains constant for the temperature range 298°k to 353°k. Afler 353°k, χ (T) considerably increases with temperature.

SUMMARY

The study of physical properties of amorphous semiconductors has become an active field in solid state physics over the last decade. In perticular, the nature of electronic transport in these material has attracted much attention during recent years.

When low electric field is applied to multicomponent chalcogenide glasses, the current is ohmic and material is in an almost nonconductive state. The resistivity of the material lies typically in the range $10^8 - 10^{10} \Omega$cm at room temperature.

It is observed that, for our sample, the resistivity lies in the range $10^4 - 10^5 \Omega$ cm at room temperature. This considerable decrease in resistivity may be due to annealing of samples. For the study of I-V characteristics, dc electrical conductivity, thermoelectric power and magnetic susceptibility measurement we have used the annealed samples. Due to annealing homonuclear bonds break and more heteronuclear bonds are formed. This results finally in to an ordered structure. The band gap of the material is decreased, and therefore conductivity increases.

For our samples, the study of I-V characteristics shows that, at a certain perticular voltage, for each sample, breakdown occurs. The resistance drops drastically and the material is converted in a very short time from a highly

resistive into a highly conductive state. When the voltage is decreased, the material revert back to its original state.

It is found that the electrical conductivity decreases with increase in, Indium concentration. This type of behaviour may be due to the formation of Indium oxide layers in to the bulk of the material. This may happen due to annealing. Experimentally, it is found that, oxidation layer is not formed at the interface between electrodes and sample, which altimately supports to the formation of oxide layers in to the bulk.

The difference in activation energy, calculated from the conductivity and thermoelectric power measurement, i.e. EQ ≈ 0.1 eV. This is in good agreement with the reported values by overhof and Beyer, for chalcogenide glasses.

Introduction of Indium in Se-Te system also affects the magnetic properties of the system. Experimental values of χ_{dia} supports to the dependence of χ on Z, the atomic number.

There must be some structural differences between the same material prepared by different methods and care is obviously necessary in any comparison of properties.

TABLE NO. 3.1

Values of activation energy $E\sigma^*$, E_S^* the intercept 'C', room temperature conductivity $\sigma\ \Omega^{-1}cm^{-1}$, Energy difference E_Q, the factor Qo, preexponential factor σ_0, and inelastic diffusion length l_1 for bulk of the sample $Se_{70}-Te_{30}$, $-Se_{70}-Te_{30-x}In_x$.

Glass Composition	Concentration X in% atomic Wt.	Activation Energy E_σ^* eV	Activation Energy E_S^* eV	Intercept $C\ \Omega^{-1}cm^{-1}$	Room Temp. conductivity $\sigma\ \Omega^{-1}cm^{-1}$	Energy difference $E_Q=E_\sigma^*-E_S^*$	Factor Qo	Pre-exponential factor $\sigma_0\ \Omega^{-1}cm^{-1}$	Inelastic diffusion length of hole L_1 cm
$Se_{70}-Te_{30}$	0	0.3505	0.2309	0.81×10^{-3}	3.5×10^{-9}	0.12	1.9	20.83	27.80×10^{-10}
$Se_{70}-Te_{29}In_1$	0.1	0.3629	0.2505	0.79×10^{-3}	5.4×10^{-9}	0.11	1.8	19.85	26.5×10^{-10}
$Se_{70}-Te_{27}In_3$	0.3	0.3862	0.2946	0.69×10^{-3}	1.3×10^{-10}	0.09	1.76	17.90	23.9×10^{-10}
$Se_{70}-Te_{25}In_5$	0.5	0.3972	0.3086	0.52×10^{-3}	2.9×10^{-10}	0.088	1.55	17.10	22.9×10^{-10}
$Se_{70}-Te_{23}In_7$	0.7	0.4285	0.3491	0.26×10^{-3}	2.5×10^{-11}	0.08	1.53	15.60	20.8×10^{-10}

REFERENCES

1. H. Kahnt and A. Feltz, J. Non. Cryst. Solids 41, 86(1986).
2. Kastner M. and Hudgens, S.J., Philo. Mag. B, (GB) 37, 665 (1978).
3. Haisty, and Krobs. Phys. Status Solid A, 59 (1986) 505-12.
4. Davis, E.A., Mott, N.F. Electronic Process in Non Crystalline Materials. Oxford Univ. Press, New York (1977).
5. Majid, C-A. Philo. Mag. B. 49 (1984) 1-3.
6. Fritzsche, H. J. Non Cryst. Solids 6, 49 (1971).
7. Nagles, P. Calloerts A., Denayer M. Proceding of eleventh international conference on physics of semiconductors, edited by Miasek M. (Amsterdam Elsevier) P. 549 (1972).
8. F.R. Shapiro and D. Adler, J. Non cryst. solids 66, 303 (1984).
9. Overhof, H. and Beyer, W. Philo. Mag. B. 49, Lg (1984).
10. Seager, C.H., Emin, D. and Quinin R.K. phys. Rev. B 8, 4746 (1973).
11. Mott N.F., J. Non-Cryst. solid 77,78 115-120 (1985).
12. Nagles, P. phy. status solid A 59, 2 (1986) 505-12.
13. Mott N.F., philo. mag. B.49 (1984) L75.
14. Cutter, M. and Mott N.F. phy. Rev. 181, 1336 (1964).
15. "Physical properties of Amorphous Materials." Editer by D. Adler, B.B. Schwartz, and M.C. Steele, Plenum Press, New York and London (1985).