DETERMINATION OF D. C. CONDUCTION PARAMETERS IN a-$Se_{100-x}Bi_x$ THIN FILMS

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Temperature dependence of d. c. conductivity is studied in a-$Se_{100-x}Bi_x$ thin films, where x is varied from 0.5 to 6 in the temperature range (255 K to 360 K).Two regions have been observed in the entire temperature range. The first region is in the temperature range (308 K-360 K) which is known as high temperature region and the second region is in the temperature range (255 K-305 K) which is low temperature region. The conductivity curve in the first region shows the exponential increase in conductivity with temperature having single activation energy. Electrical parameters have been calculated for each sample in this region. It has been observed that the activation energy decreases on increasing the concentration of Bi in a-$Se_{100-x}Bi_x$. Composition dependence of conductivity shows that conductivity first decreases with increase in Bi concentration and thereafter increases on increasing concentration of Bi. In low temperature range (II region), variable range hopping conduction is observed. Mott parameters and density of localized states near Fermi level have been calculated. The results indicate that the density of localized states increases on increasing concentration of Bi in a-$Se_{100-x}Bi_x$.

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1. Introduction

Chalcogenide glasses have found application in resistance switching [1], which can be used as ON and OFF switch if switching is of threshold type. However, the glasses can be used for memory application if switching is of memory type. Such a memory effect is being used in computer memories. Application of chalcogenide glasses have also been reported in the civil, medical and military areas [2-4] It is possible to produce electrical switches, xerographic and thermoplastic media, photo- resistant and holographic media, optical filters, optical sensors, waveguides, non-linear elements, etc. [5-8].

It has been found that Se based alloys are more useful as compared to pure Se, due to their grater hardness, high photosensitivity, higher crystallization temperature and smaller aging effect as compared to pure a-Se [9]. The addition of impurities to disordered systems has a pronounced effect on changing their conduction mechanisms and their structures. This effect can be widely different for different impurities. Several workers [10-12] have reported the impurity effects in various chalcogenide glasses. Due to ease of fabrication and processing, they are interesting as core materials for optical fibers used for transmission especially when short length and flexibility are required [13-14]. Since the advent of electrophotography, amorphous selenium has become a material of commercial importance. Selenium exhibits the unique property of reversible phase transformation [15]. Its various device applications like rectifiers, photocells, vidicons, xerography, switching and memory etc. have made it attractive, but pure selenium has disadvantages like short lifetime and low photosensitivity. This problem can be overcome by alloying Se with some impurity atoms such as Bi, Te, Ga, Sb, As, Pb which give higher

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photosensitivity, higher crystallization temperature and smaller ageing effects [16-18]. These glasses generally exhibit p-type electrical conduction due to the pinning of the Fermi level arising from the trapping of the charge carriers at localized gap states [19-20]. But in 1979, Tohge et al. [21-22] reported for the first time p-to n-type transition in Bi doped Ge-Se glasses at higher concentration of Bi (more than 7 at %). Due to this reason, the Bi doping becomes important in chalcogenide glasses. The present paper reports the electrical measurements in $Se_{100-x}Bi_x$ glassy system to calculate some important electrical parameters at low and high temperature range.

2. Experimental details

2.1 Synthesis of materials

Glassy alloys of $Se_{100-x}Bi_x$(x = 0.5, 2.5, 4, 6) were prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Bi elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated (~10^{-5} Torr) quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm). The ampoule containing material was heated to 800 ^{0}C and was held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3 - 4 ^{0}C / minute. During heating, the ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. This was done to obtain homogeneous glassy alloys. After rocking for about 12 hours, the obtained melt was rapidly quenched in ice-cooled water. The quenched sample was then taken out by breaking the quartz ampoule.

2.2 Thin films preparation

Thin films of the glassy material were prepared by vacuum evaporation technique keeping glass substrate at room temperature. Vacuum evaporated indium electrodes at bottom were used for electrical contacts. The thickness of the films was ~ 500 nm. The coplanar structures (length ≈ 1.2 cm and electrode separation ≈ 0.5mm) were used for the present measurements (see Fig.1).

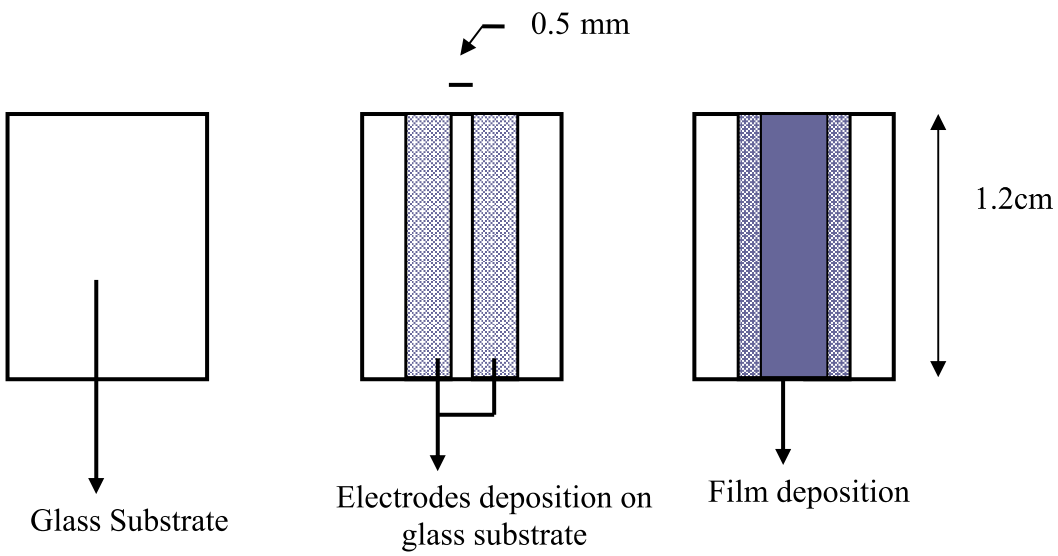

Fig.1 Co-planer structure of thin film.

For the measurement of electrical conductivity, thin film samples were mounted in a specially designed sample holder (see Fig.2) which has a transparent window to shine light for these measurements in a vacuum ~10^{-3} Torr. The temperature of the films was controlled by mounting a heater inside the sample holder and measured by a calibrated copper - constantan thermocouple mounted very near to the films. The low temperature was obtained by cooling the samples using liquid nitrogen.

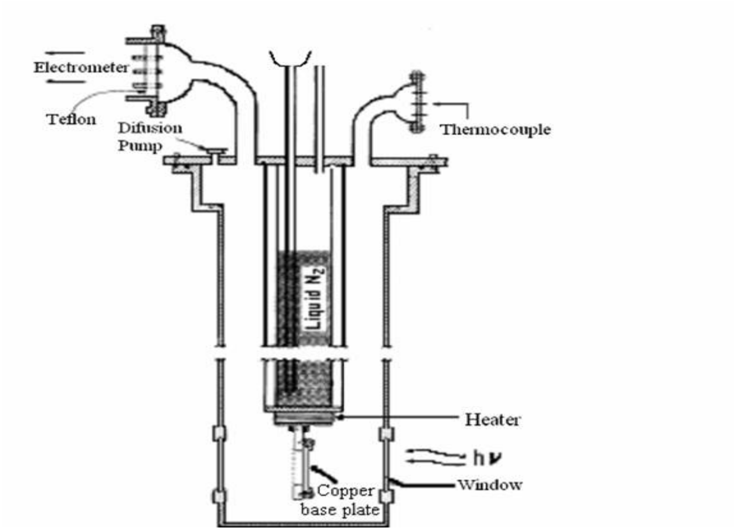

Fig.2 Cryostat used for the measurements of conductivity at different temperatures in vacuum.

The resistance is measured by a digital Electrometer (Keithley, model 614) and conductivity has been calculated by the relation:

$$\sigma_{dc} = (1/R)\,(L/A) \qquad (1)$$

Where, R is resistance of the sample, L is the thickness of the sample; A is the area of cross-section of the sample.

The heating rate was kept quite small (0.5 K/min) for these measurements. Before measuring the dark conductivity, the films were first annealed below glass transition temperature T_g for two hours in a vacuum ~ 10^{-3} Torr. I-V characteristics were found to be linear in all the glasses studied. The present measurements were made by applying only 10 V across the films.

3. Results and discussion

The measurements of the temperature dependence of d c. conductivity have been performed in a-$Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4 & 6) thin films. Fig. 3 shows the temperature dependence of dark conductivity in a-$Se_{100-x}Bi_x$ thin films, in the entire temperature range 255 K – 360 K. On the basis of the nature of slope it is clear that the temperature region is divided into two regions for each sample except $Se_{94}Bi_6$ thin films.

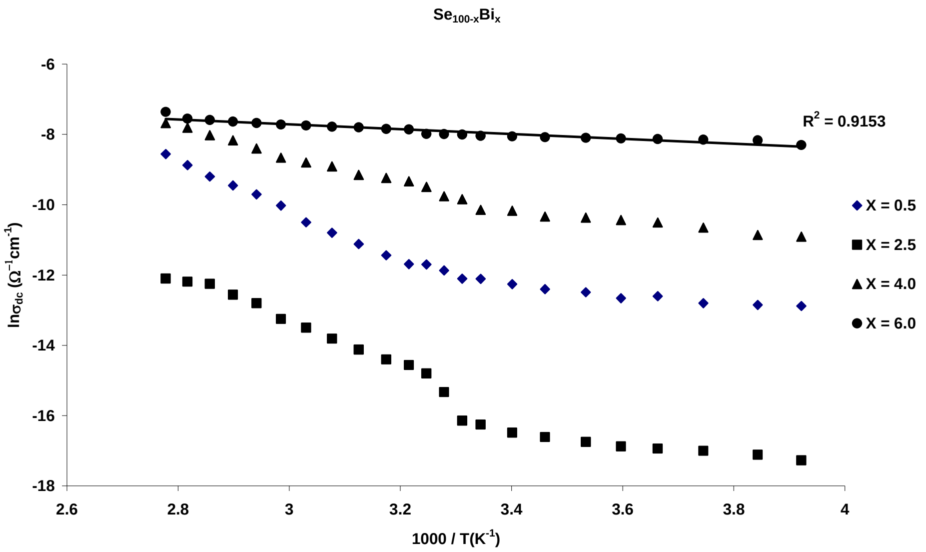

Fig.3 Temperature dependence of conductivity plotted as lnσ_{dc} versus 1000 / T in a- $Se_{100-x}Bi_x$ thin films.

In the temperature range (308 K-360 K) (Region I), the conductivity curve shows the exponential nature of the conductivity following the relation:

$$\sigma_{dc} = \sigma_0 \exp(- \Delta E / k T) \tag{2}$$

where, ΔE is the activation energy for conduction and k is the Boltzmann's constant.

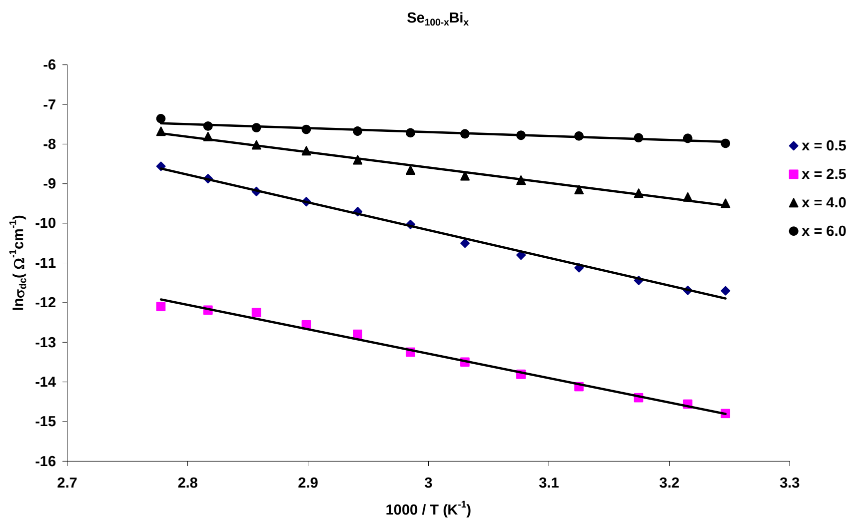

Fig 4. Temperature dependence of conductivity in high temperature range (region I)

The ln σ_{dc} vs 1000 / T curve is a straight line in this temperature range which is shown in Fig. 4. This may be associated with the increase of charge carrier concentration in extended states on increase of temperature due to extended state conduction. The values of conductivity σ_{dc} at a particular temperature 308 K, pre-exponential factor σ_0 and ΔE for different compositions of $Se_{100-x}Bi_x$ glassy alloys are given in Table1. It is clear from this table that ΔE decreases with increase in Bi concentration (see Fig.5) which may be due to a decrease in band gap. However, the composition dependence of conductivity shows that conductivity first decreases with increase in Bi concentration and thereafter increases on further increase in Bi concentration in a-$Se_{100-x}Bi_x$ which is shown in Fig.6. Reasons for such a minimum at % 2.5 can not be understood from the present measurements

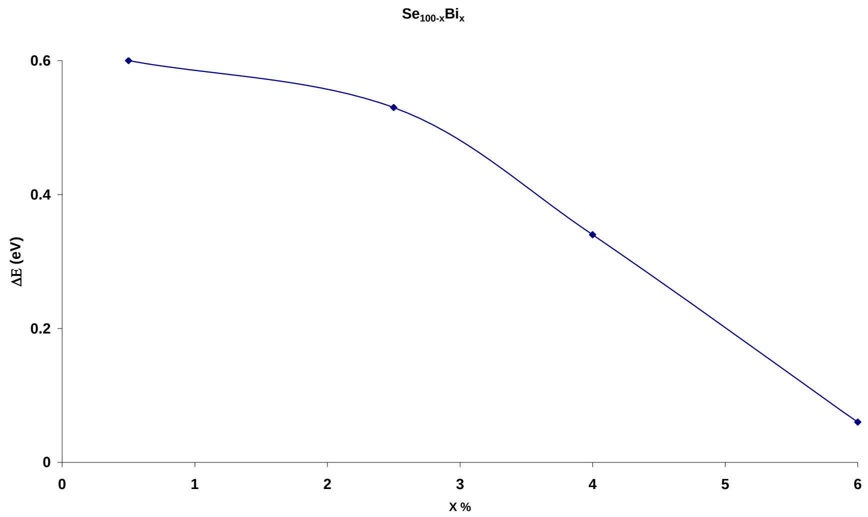

Fig. 5 Composition dependence of activation energy in a- $Se_{100-x}Bi_x$

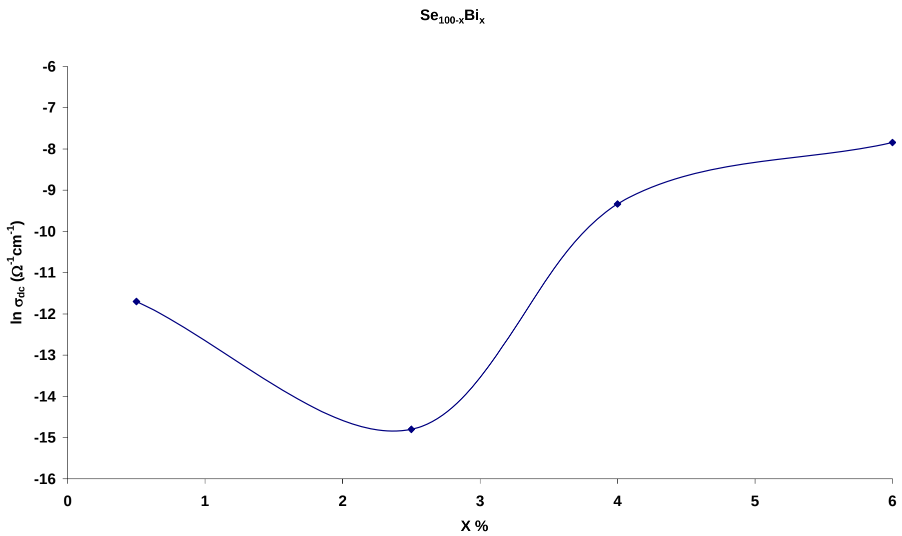

Fig.6 Composition dependence of d. c conductivity at 308 K in a- $Se_{100-x}Bi_x$

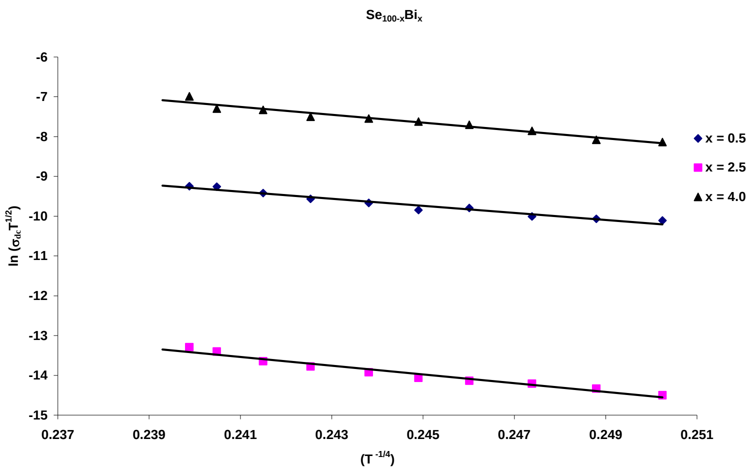

Fig.7 ln ($\sigma_{dc} T^{1/2}$) vs. $T^{-1/4}$ plot in a- $Se_{100-x}Bi_x$ thin films (region II).

In region II (255K-305 K), the slope of straight line gradually decreases but another straight line can be fitted in this temperature range. In such a case, the conduction can be attributed to the hopping of the charge carriers between localized states near Fermi level and the conductivity can be expressed as [23-24]:

$$\sigma_{dc} T^{1/2} = \sigma_1 \exp (AT^{-1/4}) \tag{3}$$

and

$$A^4 = T_0 = \lambda\alpha^3 / k\, N(E_F) \tag{4}$$

where $N(E_F)$ is the density of localized states at E_F, α^{-1} the degree of localization, T_0 the degree of disorder. λ and A are dimensionless constants. The value of pre-exponential term σ_1 of eq.2 as obtained by various workers is given by

$$\sigma_1 = 3e^2 \gamma\, [N (E_{F)} / 8\pi\alpha kT]^{1/2} \tag{5}$$

where 'e' is electronic charge and the 'γ' Debye frequency (=10^{13} Hz). A simultaneous solution of eq.(3) and (4) yields

$$\alpha = 22.52\sigma_0 A^2 (cm^{-1}) \tag{6}$$

and

$$N(E_F) = 18\, \alpha^3 / k\, A^4 \; (cm^{-3}eV^{-1}) \tag{7}$$

The hopping distance and hopping energy is given by

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

$$W = 3/4\, \pi R^3 N(E_F) \tag{9}$$

To see the applicability of Mott's variable range hopping (VRH) conduction model in our case we have plotted a graph between ln $\sigma_{dc} T^{1/2}$ vs $T^{-1/4}$ which is found to be a straight line (see Fig.7) indicating the validity of hopping conduction mechanism. This is in good agreement with Mott's VRH model. The slope of this curve gives the value of N (E_F). Other Mott's parameters are calculated from eq. (3 -9) and are given in Table 2. It is evident from Table 2 that the density of localized states increases with increase in Bi concentration in a- $Se_{100-x}Bi_x$.

Table1. D.C. conduction parameters in the high temperature range in a- $Se_{100-x}Bi_x$

Bi (%)	σ_{dc} ($\Omega^{-1}cm^{-1}$) at 308 K	ΔE (eV)	σ_0 ($\Omega^{-1}cm^{-1}$)
0.5	8.29 x 10^{-6}	0.60	4.85 x 10^{4}
2.5	3.74 x 10^{-7}	0.53	1.78 x 10^{2}
4.0	8.84 x 10^{-5}	0.34	2.09 x10^{1}
6.0	3.92 x 10^{-4}	0.06	2.73 x 10^{2}

Table 2. Mott^s Parameters in the low temperature region in a- $Se_{100-x}Bi_x$

Bi (%)	A ($K^{1/4}$)	T_0 (K)	$N(E_F)$ ($eV^{-1}cm^{-1}$)	α x 10^6 (cm^{-1})	R (cm)	W (eV)	αR
0.5	88.63	6.17 x 10^{7}	3.20 x10^{16}	2.12	3.75x10^{-6}	0.140	7.95
2.5	109.72	1.45 x 10^{8}	6.14 x10^{16}	3.49	2.81x10^{-6}	0.174	9.84
4.0	98.54	9.43 x 10^{7}	1.03 x10^{17}	3.60	2.45x10^{-6}	0.156	8.84
6.0	-	-	-	-	-	-	-

The chalcogenide glassy semiconductors show continuous change of physical properties with change in chemical composition. These structural changes in the network may induce modification in the density and distribution of localized states in the semiconductor system. The net effect of these modifications is to increase the defect density participating in the electrical transport as observed in the present case.

4. Conclusions

The present paper reports the measurements of conductivity as a function of temperature. In high temperature region, conductivity is thermally activated having single activation energy. Electrical parameters such as activation energy (ΔE) and pre-exponential factors σ_o have been calculated for each sample. It has been observed that the activation energy decreases on increasing concentration of Bi. Composition dependence of conductivity shows that conductivity decreases at 2.5% of Bi. However on further increase in Bi, conductivity increases.

Conductivity data in the low temperature region has been used to determine the density of states near Fermi level using the theory of variable range hopping conduction. The results indicates that the density of localized state increases with increase in Bi concentration in a- $Se_{100-x}Bi_x$

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