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Space charge limited conduction in a-$Ge_{20}Se_{80}$ and a-$(Ge_{20}Se_{80})_{95}Ga_5$ glassy alloys

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Trap depth and density can be determined from the analysis of the dependence of space charge limited currents (SCLC) on applied electric field. Thin films of a-$Ge_{20}Se_{80}$ and a-$(Ge_{20}Se_{80})_{95}Ga_5$ have been deposited by thermal evaporation technique at a base pressure ~ 2×10^{-5} mbar and room temperature (300 K). Current (I)–Voltage (V) characteristics have been measured at different temperatures. These curves show nearly linear dependence at low voltages and afterwards a non-linear behaviour at higher voltages. Detailed studies of I-V curves indicate the ohmic conduction at low voltages and trap limited SCLC at higher voltages. From fitting of the data, the density of defect states (DOS) near Fermi level is calculated.

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1. Introduction

The electrical and optical properties of III-VI compounds are strongly influenced by the presence of carrier trapping centers in the forbidden gap, arising from the native defect states. The study of these compounds involves the investigation of physical properties for device applications. These properties, strongly affect the device performance, depending upon the deposition techniques and conditions [1,2]. The understanding of the electrical parameters of the material, strongly influenced by the presence of energy levels in the forbidden gap, is essential for device studies. When a sufficiently large field is applied to highly resistive material with ohmic contacts, electrons will be injected into the bulk to form a current which is limited by space charge effects. When trapping centers are present, they capture many of the injected carriers, thus reducing the density of free carriers. The SCLC measurement is an invaluable tool for determining low concentrations and energy distributions of carrier trapping states in amorphous materials [3]. The energy width of the traps can be measured from the super quadratic slope in the I-V curves as high field effects are most readily observed in amorphous materials because of their low conductivity (Joule heating is negligibly small at moderate temperatures). The results of these effects are interpreted in terms of heating effect, SCLC and high field conduction due to Poole-Frenkel effect which indicates that the interpretation of the high field data is highly intriguing in these materials and much has to be done in this field.

Thin film technology is well established and widely used in the fabricating of electronic devices. This technique has been successfully used to fabricate thin film resistors, capacitors, photo electronic devices etc. [4-7]. The use of this technique in fabricating electronic devices makes it necessary to understand the electrical properties of the material in thin film form. The effect of incorporation of third element in binary chalcogenide glasses has always been an interesting problem in getting relatively stable glassy alloys as well as to change the conduction from p to n type. In Ge-Se system, some metallic additives have been found to change conduction from p-type to n-type and hence this binary system is of great importance.

Ge-Se is known to be very good covalently bonded glass formers. The structure of these glasses is a function of composition [8-10]. A discontinuity in various physical properties of these glasses has been observed at a composition when the average coordination number $<r>$ = 2.4 [11]. At x = 20, the value of $<r>$ is 2.4 in a-Ge_xSe_{100-x} system. In the Se rich zone, the structure consists of Se chains linked by Ge atoms tetrahedrally coordinated by Se atoms i.e. the structure consists of chains of corner shared $GeSe_{4/2}$. As the Ge concentration increases, the corner shared tetrahedrons give place to edge shared ones [8-10]. It has been reported that at a concentration about 20 at. % of Ge, a new non-crystalline compound $GeSe_4$ exists in the Ge-Se system [12]. Boolchand *et al.* [13] have also observed the evidence of two rigidity transitions as monitored by compositional trends in corner-sharing (ν_{CS}) and edge-sharing (ν_{ES}) $Ge(Se_{1/2})$ mode frequencies in Ge_xSe_{1-x} glasses at $0 < x < 1/3$ by Raman scattering measurements. A second order transitions from a floppy to an unstressed rigid phase occurs near x = 0.20, where both $\nu_{CS}(x)$ and $\nu_{ES}(x)$ show a kink. What happens to the $Ge_{20}Se_{80}$ system, when it is alloyed with a second element of group III, is very important from the basic as well as application point of view. Ga belongs to the III group and its atomic radii (1.35Å) is more than the Ge (1.22 Å).

Therefore, the authors have decided to study the effect of Ga additive on the SCLC mechanism in such a technically important material. The experimental details and the characteristics of the samples are described in Section 2. The results have been presented and discussed in section 3. The last section deals with the conclusions of the present work.

2. Experimental

Glassy alloys of $Ge_{20}Se_{80}$ and $(Ge_{20}Se_{80})_{95}Ga_5$ are prepared by melt quenching technique. Materials (99.999% pure) are weighed according to their atomic wt. percentages and are sealed in quartz ampoules in a vacuum ~ 2×10^{-5} mbar. The sealed ampoules are kept inside a furnace where the temperature is increased up to 1050 K. The ampoules are frequently rocked for 24 hours at the highest temperature to make the melt homogeneous. The quenching is done in liquid nitrogen. Thin films of these alloys are prepared by vacuum evaporation technique keeping substrates at room temperature and base pressure of ~ 2×10^{-5} mbar using a molybdenum boat. Pre-deposited thick indium electrodes with different electrode gaps on well-degassed corning 7059 glass substrates are used for the electrical contacts. A planar geometry of the film is used for electrical measurements. The thickness of the films is ~ 500 nm. The films are kept in the deposition chamber in dark for 24 hours before mounting them in the metallic sample holder to attain thermodynamic equilibrium. The electrical conductivity of the amorphous films is studied by mounting them in a specially designed metallic sample holder. A vacuum of about 10^{-3} mbar is maintained throughout these measurements. The results are found to be the same in higher vacuum ~10^{-5} mbar also which have been verified in the laboratory. The accuracy in dark current, measured by picoammeter (DPM-111), is 1pA. The films are annealed at 353 K for 2 hours in a vacuum of about 10^{-3} mbar and the dark conductivity measurements are carried out.

3. Results and discussion

The results of I-V characteristics at different temperatures show ohmic behavior at low voltages (up to 110 V) in both glassy samples studied here. However, at higher voltages (E ~ 10^4 V/cm), a super ohmic behaviour has been observed in both samples. Fig. 1 shows Ln I/V versus V curves, which are found to be straight lines in case of *a*-$Ge_{20}Se_{80}$ and *a*-$(Ge_{20}Se_{80})_{95}Ga_5$ with the electrode gap (L) = 0.24 mm. Similar results for both samples have been observed at other electrode gaps also.

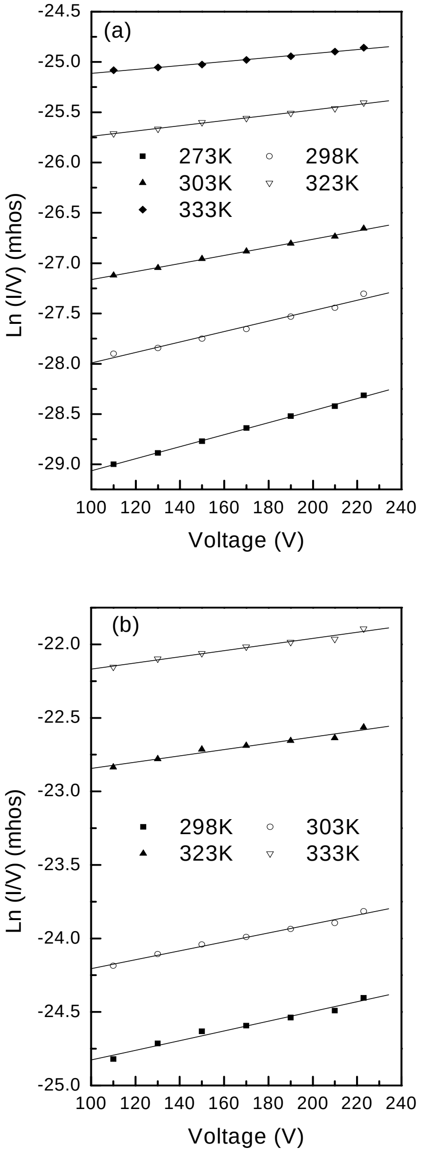

Fig. 1. Plots of Ln(I/V) vs. V for (a) $Ge_{20}Se_{80}$ and (b) $(Ge_{20}Se_{80})_{95}Ga_5$ with electrode gap (L) = 0.24 mm.

According to the theory of SCLC, in the case of a uniform distribution of localized states, the current (I) at a particular voltage (V) is given by [14]

$$I = \left(\frac{2eA\mu N_0 V}{L}\right)\exp(SV) \qquad (1)$$

here, e is the electronic charge, A is the cross sectional area of the film, N_o is the density of free charge carriers, L is the electrode spacing and S is given by:

$$S = \frac{2\varepsilon_r \varepsilon_0}{e g_0 k T L^2} \qquad (2)$$

where ε_r is the static value of the dielectric constant, ε_0 is the permittivity of free space, k is Boltzman's constant and g_0 is the density of localized states.

Table 1. Composition dependence of density of localized states (g_0) in $Ge_{20}Se_{80}$ and $(Ge_{20}Se_{80})_{95}Ga_5$ glassy alloys at 300 K.

Glassy alloys	Slope of S vs. 1000/T curves	ε_r (at 2 kHz, 300 K)	g_0 ($eV^{-1}cm^{-3}$)
$Ge_{20}Se_{80}$	4.3×10^{-3}	6.30	3.85×10^{13}
$(Ge_{20}Se_{80})_{95}Ga_5$	2.7×10^{-3}	6.73	3.70×10^{13}

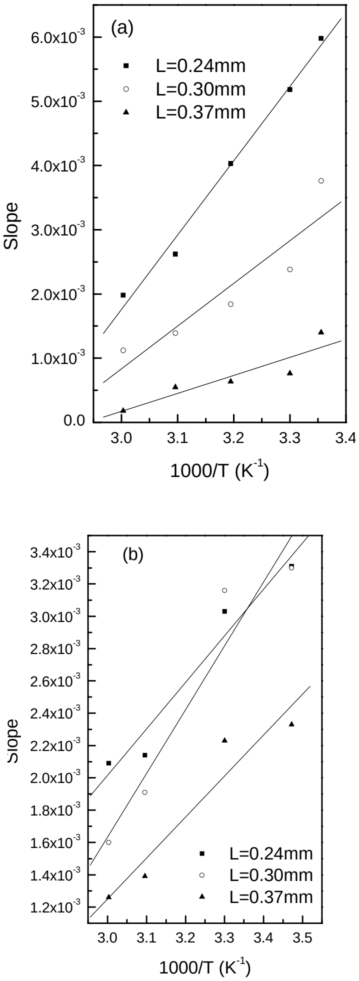

Fig. 2. Plots of slope vs. 1000/T for (a) $Ge_{20}Se_{80}$ and (b) $(Ge_{20}Se_{80})_{95}Ga_5$ at different electrode gaps.

According to equation (1), Ln (I/V) vs. V curves should be straight lines whose slope should decrease with increase in temperature [(from equation (2)]. Figure 2 shows the plots of Slope (S) vs. 1000/T for a-$Ge_{20}Se_{80}$ and a-$(Ge_{20}Se_{80})_{95}Ga_5$ glassy alloys at different electrode gaps. The slope decreases with increase in temperature at all gaps. Using the slope of figure 2 and equation (2), the density of localized states (g_0) has been calculated. The results of these calculations are given in Table 1. The value of the relative dielectric constant (ε_r) has been measured at different temperatures by using capacitance measuring assembly (Model: GR1620) by three terminal technique.

Table 2. Values of slopes of Ln I/V vs. V curves for different electrode gaps in $Ge_{20}Se_{80}$ and $(Ge_{20}Se_{80})_{95}Ga_5$ glassy alloys at 300 K.

Electrode gap (L) (mm)	$1/L^2$ (mm^{-2})	slope of Ln I/V vs. V curve for $Ge_{20}Se_{80}$	slope of Ln I/V vs. V curve for $(Ge_{20}Se_{80})_{95}Ga_5$
0.24	17.36	6.31×10^{-3}	2.88×10^{-3}
0.30	11.11	4.00×10^{-3}	2.75×10^{-3}
0.37	07.31	2.81×10^{-3}	2.54×10^{-3}

According to Goswami [15], a plot of LnI vs. 1000/T in SCLC region will give the trap depths. Figure 3 shows LnI vs. 1000/T curves for a-$(Ge_{20}Se_{80})_{95}Ga_5$. Similar curves have been observed for a-$Ge_{20}Se_{80}$ alloy (results not shown here) also. The trap depths corresponding to each electrode gap are calculated which are found to be lying between 0.52-0.85 eV for a-$Ge_{20}Se_{80}$ and 0.54-0.57 eV for a-$(Ge_{20}Se_{80})_{95}Ga_5$.

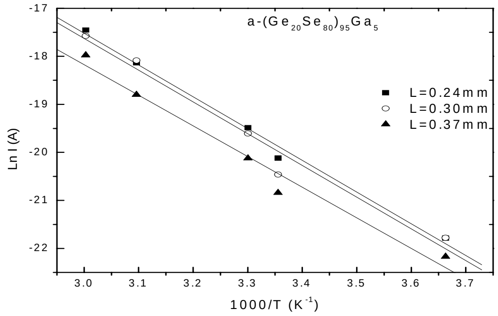

Fig. 3. Plots of Ln I vs. 1000/T for a-$(Ge_{20}Se_{80})_{95}Ga_5$ at different electrode gaps.

In amorphous materials, non-ohmic behavior has also been explained in terms of high field conduction due to the Poole-Frenkel effect of screened charge intrinsic defects and field induced lowering of energy barriers for the charge-carrier hopping within localized states at the band edges [16-18], according to which the current I at a particular voltage V is given by:

$$LnI = \frac{e\beta V^{1/2}}{kTL^{1/2}} + \text{constant} \tag{3}$$

The theoretical value of β is given by

$$\beta = \left(\frac{e}{\pi \varepsilon_r \varepsilon_0} \right)^{1/2} \tag{4}$$

According to equation (3), LnI vs. $V^{1/2}$ curves should be straight lines at a particular temperature of measurement. The slope should however, decrease with increasing temperature.

Fig. 4 shows the plots of LnI vs. $V^{1/2}$ at various temperatures at L = 0.24 mm. The observed trend verifies the validity of equation (3). To distinguish between these two processes, the plots of Ln I/V vs. V must be independent of the electrode spacing 'L'. On the other hand, for any SCLC mechanism, the slopes of the same plot are dependent on the values of 'L'. We have therefore plotted I-V curves at room temperature (300 K) for samples having different electrode gaps. The results for a-$Ge_{20}Se_{80}$ and a-$(Ge_{20}Se_{80})_{95}Ga_5$ are plotted in figure 5. We obtain different slopes at different electrode gaps which overrules the Poole-Frenkel effect and confirms the presence of SCLC mechanism in these glassy alloys. The values of these slopes are given in Table 2.

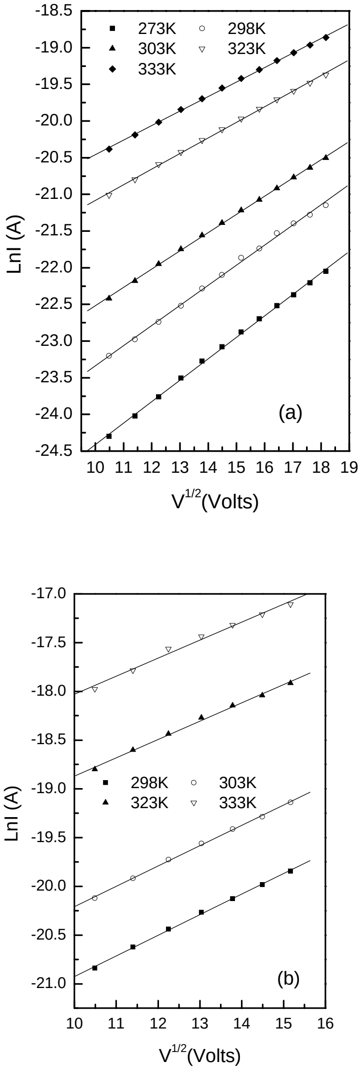

Fig. 4. Plots of LnI vs. $V^{1/2}$ for (a) $Ge_{20}Se_{80}$ and (b) $(Ge_{20}Se_{80})_{95}Ga_5$ with electrode gap (L) = 0.24 mm.

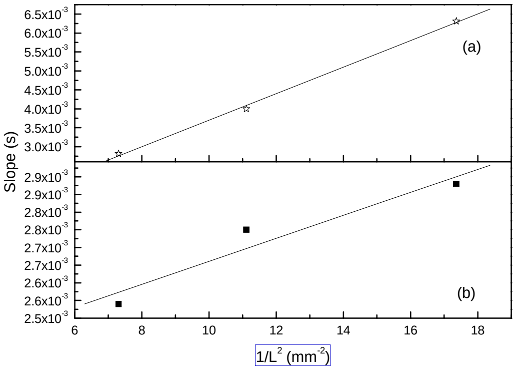

Fig. 5. Plots of s vs. $1/L^2$ for (a) $Ge_{20}Se_{80}$ and (b) $(Ge_{20}Se_{80})_{95}Ga_5$.

The density of states decreases after the addition of Ga into a-$Ge_{20}Se_{80}$ alloy which can be explained on the basis of structural changes. The structure of a-Ge-Se-Ga glasses is made up from tetrahedral $GeSe_2$ and pyramidal Ga_2Se_3 units [19]. According to the chemically ordered covalent network model [20], the $GeSe_2$ and Ga_2Se_3 units are connected with extra Se atoms. The excess Se atoms are connected in chains. The bond energy of GaSe bonds (65 kcal/mol) is larger than GeSe bond energy (55.4 kcal/mol), which indicates that by the addition of Ga content, the average bond energy of the system will increase [21]. The formation of stronger bonds after Ga addition could be the cause of the decrease of density of localized states (g_0) in a- $Ge_{20}Se_{80}$ alloy.

4. Conclusion

I-V characteristics have been studied in amorphous thin films of $(Ge_{20}Se_{80})_{1-x}Ga_x$ (with x = 0, 5 at %). At low fields, ohmic behavior is observed. However, at higher fields (~10^4 V/cm) super ohmic behavior is observed. Analysis of the observed data shows the existence of SCLC in the glassy samples used in the present study. From the fitting of the data in the theory of SCLC, the density of localized states (g_0) near Fermi-level is calculated. The observed decrease in g_0 has been discussed in terms of structural changes occurred in Ge-Se-Ga glassy system.

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