Composition dependence of density of states in a-Se$_{100-x}$Sn$_x$ thin films

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Abstract. The present paper reports the DC conductivity measurements at high electric fields in vacuum evaporated amorphous thin films of a-Se$_{100-x}$Sn$_x$ ($x = 0, 2, 4, 6$) glassy alloys. Current–voltage (I–V) characteristics have been measured at various fixed temperatures. In these samples, at low electric fields, ohmic behaviour is observed. However, at high electric fields ($E \sim 10^4$ V/cm), non-ohmic behaviour is observed. An analysis of the experimental data confirms the presence of space charge limited conduction (SCLC) in the glassy materials studied in the present case. From the fitting of the data to the theory of SCLC, the density of defect states (DOS) near Fermi level is calculated. Increase in DOS with increase in Sn concentration has been found which could be correlated with the electronegativity difference between the two elements used here in making the glassy alloys. The peculiar role of the element Sn as an impurity in the pure Se glassy alloy is also discussed.

Keywords. Chalcogenide glasses; localised states; space charge limited conduction; high field conduction.

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1. Introduction

Amorphous selenium has been emerged as a promising material because of its potential technological importance. It is widely preferred in the fabrication of electrophotographic devices and more recently in switching and memory devices [1]. It has been found that Se-based alloys are useful because of its greater hardness, high photosensitivity, higher crystallisation temperature and smaller ageing effect compared to pure a-Se [2]. The transport mechanism of charge carriers in amorphous semiconductors has been the subject of intensive theoretical and experimental investigations for the last few years. These studies have been stimulated by the attractive possibilities of using the structure disorder in amorphous semiconductors for the development of better, cheaper and more reliable solid state devices [3,4].

Due to their low conductivity, amorphous semiconductors are most suitable for high field conduction studies, as the Joule heating is negligibly small in these materials at moderate temperatures. Some such studies have been reported in chalcogenide glassy semiconductors [5–15] and the results have been interpreted in terms of space charge limited conduction or Poole–Frenkel conduction. One of the most direct methods for the determination of the density of the localised states g_0 in the mobility gap involves the measurements of SCLC, which can be easily observed at high fields in chalcogenide materials. Such a technique has already been applied to a-Si:H [16–19]. SCLC technique is not influenced by surface states unlike field effect experiments where surface states may come into play.

The present paper reports the SCLC measurements in an important glassy system Se–Sn, where properties have been found to be highly composition-dependent. Using the theory of SCLC, for the case of uniform distribution of localised states, the density of localised states near Fermi level is calculated for the present system.

2. Experimental

Glassy alloys of $Se_{100-x}Sn_x$ ($x = 0, 2, 4, 6$) were prepared by quenching technique. High-purity (99.999%) materials were weighed according to their atomic percentages and were sealed in quartz ampoules (length ~ 5 cm and internal diameter ~ 8 mm) with a vacuum of $\sim 10^{-5}$ Torr. The ampoules containing the materials were heated to $900°C$ and held at that temperature for 10–12 h. The temperature of the furnace was raised slowly at a rate of ~ 3–$4°C/min$. During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules are tucked away in the furnace. This was done to obtain homogenous glassy alloys.

After rocking for about 10 h, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping them to ice-cooled water. The quenched samples were taken out by breaking the quartz ampoules. The glassy nature of the materials was checked by XRD technique. Compositional analysis was performed using electron probe microanalysis (EPMA) technique.

Thin films of these glasses were prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at bottom were used for the electrical contact. The thickness of the films was ~ 500 nm. The co-planar structure (length ~ 1.2 cm and electrode separation ~ 0.12 mm) was used for the present measurements. The films were kept in deposition chamber in the dark for 24 h before mounting them in the sample holder because the alloy gets sufficient annealing at room temperature so that a metastable thermodynamic equilibrium may be attained in the samples as suggested by Abkowitz [20] for chalcogenide glasses. The deposition parameters were kept almost the same for all the samples so that a comparison of results could be made for various glassy samples. The amorphous nature of thin films was ascertained by X-ray diffraction.

For the measurements of high field conduction, thin film samples were mounted in a specially designed sample holder. A vacuum of $\sim 10^{-2}$ Torr was maintained throughout the measurements. A DC voltage (0–300 V) was applied across the sample and the resultant current was measured by a digital pico-ammeter. I–V characteristics of these films were measured at various fixed temperatures

(293–333 K). The temperature of the films was controlled by mounting a heater inside the sample holder and measured by a calibrated copper–constantan thermo-couple mounted very near to the films. Before measuring I–V characteristics, thin films were annealed in a vacuum of $\sim 10^{-2}$ Torr near glass transition temperature for 2 h in the same sample holder that was used for the above measurements.

3. Results and discussion

In the present work, I–V characteristics of thin films of a-Se$_{100-x}$Sn$_x$ ($x = 0$, 2, 4, 6) are examined at various temperatures (293–333 K). At low fields ($<10^3$ V/cm), an ohmic behaviour is observed in all the samples. However, at higher fields ($\sim 10^4$ V/cm), a superohmic behaviour is observed at all the measuring temperatures.

According to the theory of space charge limited conduction, in the case of a uniform distribution of localised states $g(E) = g_0$, the current (I) at a particular voltage (V) is given by the following relation [21]:

$$I = (eA\mu n_0 V/d)\exp(SV). \tag{1}$$

Here d is the electrode spacing, n_0 is the density of the thermally generated charge carriers, μ is the mobility, e is the electronic charge, A is the area of cross-section of thin films and S is given by

$$S = 2\varepsilon_r\varepsilon_0/eg_0 kTd^2, \tag{2}$$

where ε_r is the static value of the dielectric constant, ε_0 is the permittivity of free space, g_0 is the density of traps near the Fermi level and k is the Boltzmann's constant.

It should be noted that eq. (1) is not an exact solution of SCLC equation, but is a very good approximation of the one-carrier space charge limited current under the condition of a uniform distribution of traps. In the present case, the one-carrier assumption is justified as these glasses are known to behave as p-type material. As present measurements scan a very limited range of energy near the Fermi level, the assumption of uniform distribution of traps is also not unjustified.

As evident from eqs (1) and (2), in the case of space charge limited conduction, the $\ln(I/V)$ vs. V curves should be a straight line and slope (S) of these curves should decrease linearly with the increase of temperature.

In the present case, at higher fields, $\ln(I/V)$ vs. V curves are found to be straight lines with high correlation coefficient at all the measuring temperatures in all the samples. Such curves for amorphous thin films of Se$_{100-x}$Sn$_x$ ($x = 0$, 2,4,6) are plotted in figures 1–4 (figures 1–3 are similar to figure 4. To view these, please see http://www.ias.ac.in/pramana/v69/p681/supplement.pdf). The slope (S) of these curves decreases linearly with temperature for all the samples (see figure 5). These results indicate the presence of space charge limited conduction in all the samples used. Thin films contain a large number of defects due to dangling bonds that give rise to a large number of localised defect states. These localised states act as carrier trapping centers and after trapping the injected charge from electrodes, they become charged and thereby expected to build up a space charge. This build up of space charge then plays the key role in the determination of SCLC process.
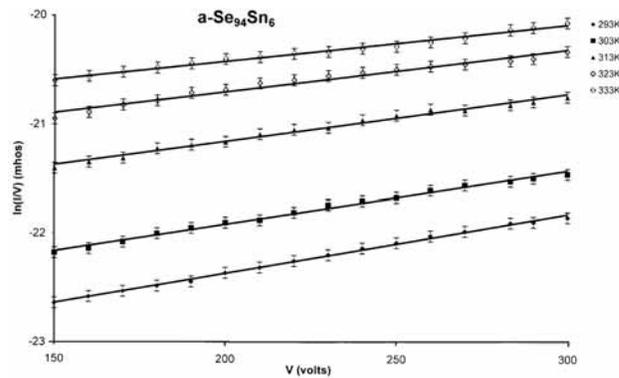
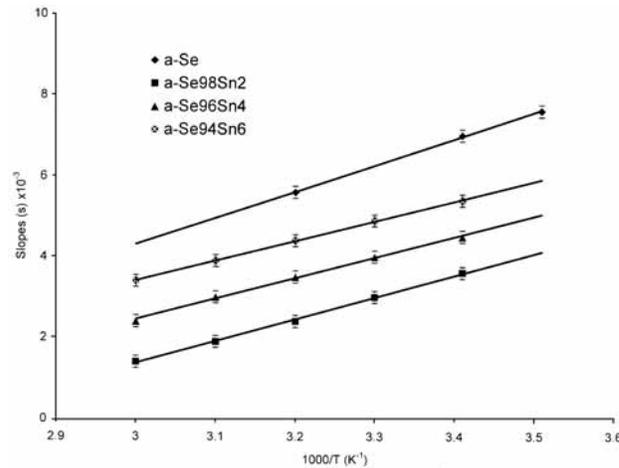**Figure 4.** Plots of $\ln(I/V)$ vs. V curves for a-Se$_{94}$Sn$_6$ films at different temperatures.

Figure 5. Plots of slope (S) of $\ln(I/V)$ vs. V curves against $1000/T$ for a-Se$_{100-x}$Sn$_x$ films.

Using eq. (2), we have calculated the density of localised states from the slopes of figure 5. The value of the relative dielectric constant ε_r are measured by using capacitance measuring assembly model GR 1620 AP, employing the three terminal technique. The results of these calculations are given in table 1 and plotted in figure 6 as a function of Sn concentration. It is clear that g_0 increases with the increase of Sn concentration in a-Se–Sn system.

When isoelectronic atom Te is added to amorphous selenium, the density of defect states increases, and hence the residual potential increases in xerographic experiment. Onozuka *et al* [22] observed that, on introducing Cl to Se–Te system, the residual potential is decreased. This result was interpreted on the basis of a structural defect model where Te was assumed to form positively charged impurities due to small electronegativity of Te as compared to Se [23], while Cl atoms
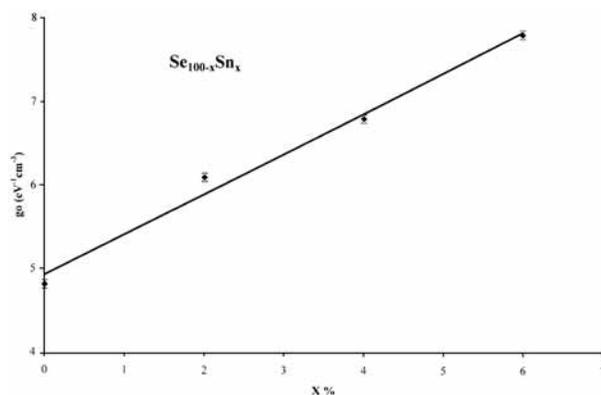
Figure 6. Plot of density of localised states (g_0) vs. Sn concentration in a-Se$_{100-x}$Sn$_x$.

Table 1. Composition dependence of density of localised states (g_o) in a-Se$_{100-x}$Sn$_x$.

Samples	Slope of S vs. $1000/T$ curve	ε_r (120 Hz ,293K)	g_o (density of localised states in eV^{-1} cm^{-3})
a-Se	6.5×10^{-3}	3.51	4.81×10^{13}
a-Se$_{98}$Sn$_2$	5.4×10^{-3}	3.67	6.10×10^{13}
a-Se$_{96}$Sn$_4$	5.1×10^{-3}	3.89	6.81×10^{13}
a-Se$_{94}$Sn$_6$	4.9×10^{-3}	4.33	7.81×10^{13}

having higher electronegativity than selenium [23] form negatively charged impurities, thereby compensating the effect of Te [22].

Along the same lines, one can expect that when Sn having lower electronegativity than Se [23] is introduced, positively charged defects are being created, thus increasing the density of defect states in the binary Se–Sn system beyond pure Se, as it is observed by us in our present measurements. We have also reported [24] similar kind of results in the case of a-Se–Sb system in our earlier measurements.

4. Conclusions

I–V characteristics have been studied in amorphous thin films of Se$_{100-x}$Sn$_x$ ($x = 0$, 2, 4, 6). At low fields ($<10^3$ V/cm), an ohmic behaviour is observed. However, at high fields ($\sim 10^4$ V/cm), a superohmic behaviour is observed.

The density of localised states near Fermi level is calculated by fitting the data to the theory of SCLC in the case of a uniform distribution of localised states. The incorporation of Sn in a-Se results in an increase in the density of localised states around the Fermi level.

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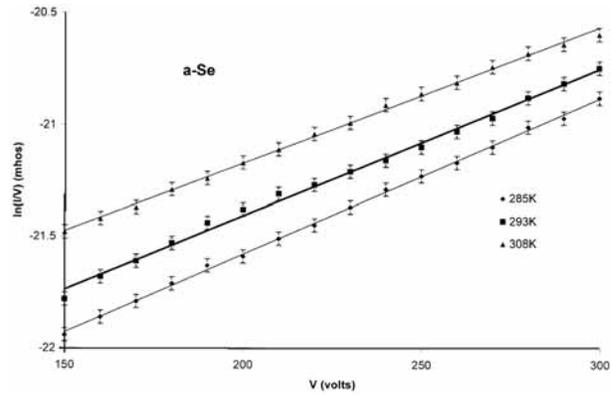
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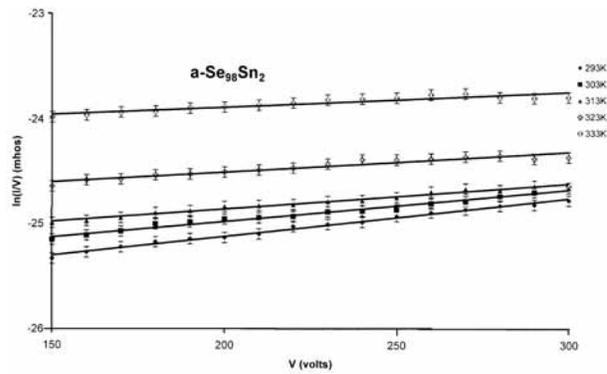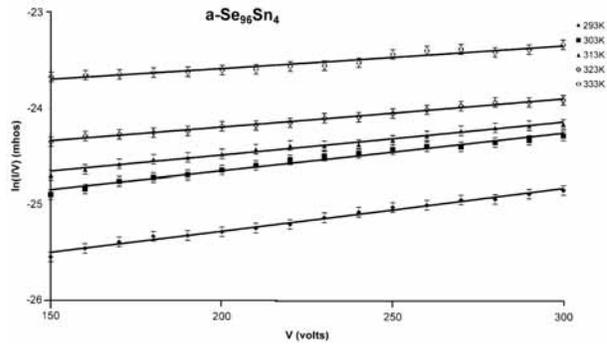**Figure 1.** Plots of $\ln(I/V)$ vs. V curves for a-Se films at different temperatures.

Figure 2. Plots of $\ln(I/V)$ vs. V curves for a-Se$_{98}$Sn$_2$ films at different temperatures.

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Figure 3. Plots of $\ln(I/V)$ vs. V curves for a-Se$_{96}$Sn$_4$ films at different temperatures.