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Effect of Ag additive on the density of localized states in Se-Ge glassy alloy

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Abstract. The present paper reports the measurements on space charge limited conduction in amorphous thin films of $Ge_{20}Se_{80-x}Ag_x$ ($x = 0$, 10, 15, 20). $I - V$ characteristics have been measured at various fixed temperatures. These characteristics show that, at low electric fields, an ohmic behaviour is observed. However, at high electric fields ($E \sim 10^4$ V/cm), the current becomes superohmic. At high fields (10^4 V/cm), current could be fitted to the theory of space charge limited conduction (SCLC) in case of uniform distribution of localized states in the mobility gap of these materials. Using the theory of SCLC for the uniform distribution of the traps, the density of localized states near Fermi level is calculated. It is observed that, on addition of Ag in $Ge_{20}Se_{80}$ alloy, density of localized states first increases till 10 at% of Ag and then decreases.

PACS. 72.80.Ng Disordered solids – 61.43.Fs Glasses – 61.43.Dq Amorphous semiconductors, metals, and alloys

1 Introduction

The properties of chalcogenide glassy semiconductors are usually affected by the addition of impurities as third element. Experimental results reported by various researchers have shown that the addition of impurity atoms in binary Se-Ge and Se-In systems does change the electrical properties of chalcogenide glasses significantly [1–3]. It has also been found that the effect of impurities depends strongly on the composition of the glass, the chemical nature of the impurity and the method of doping. Impurity concentration obviously is a critical factor in such cases because all impurities cannot behave in an electrically active manner. Several of the physical properties are found to be improved by the addition of certain impurities.

Ag-containing chalcogenide glasses have attracted widespread interest for applications in optical recording and as solid electrolytes. The importance of this combination was first established when in 1966; the effect of silver photo-diffusion in chalcogenide glasses was discovered [4]. The low free energy of crystallization of Ag (48 kcal/mol) was a further reason to consider the introduction of Ag in chalcogenide glasses used for phase change optical recording [5,6]. This enabled one for the attainment of the main requirements for good optical recording-high phase transformation rate. For this reason, the crystallization kinetics of Ag-containing chalcogenide glasses have been studied by various workers [7–9] for the development of new and better phase change recording materials. It is essential to know the properties of Ag rich chalcogenide films, especially the electrical and structural properties, since these physical properties are closely related to the mechanism of the photoinduced surface deposition (PSD) phenomena [10,11]. X-ray spectroscopic studies of Ag doped Ge-Se glasses have been studied by Shukla et al. [12] to understand the nature of bonding and concluded that bonds are iono-covalent in character. Dielectric behaviour of Ag doped Ge-Se glasses have been studied [13,14] and the dipolar behaviour is observed in these glasses. Photoconductive properties in Ag doped Se-Ge system has also been studied by Sharma et al. [15]. High field conduction in Ag doped Se-Te system has been studied by various workers [16,17]. In view of the above, we have decided to work on Ag containing Se-Ge system to study density of defect states.

The density of defect states (DOS) in chalcogenide glasses is a key parameter for determining the semiconducting properties of theses materials. To measure this quantity, different methods have been used with all their advantages and their limitations. One of the most direct methods for the determination of the density of the localized states g_0 in the mobility gap involves the measurements of SCLC, which can easily be observed at high fields

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in chalcogenide materials 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 [16–27] and the results have been interpreted in terms of space charge limited conduction or thermally assisted conduction mechanisms. The present paper reports the SCLC measurements in an important glassy system Se-Ge-Ag where properties have been found to be highly composition dependent. Using the theory of SCLC for the case of uniform distribution of localized states, the density of localised defect states near Fermi level is calculated for the present system.

2 Experimental

Glassy alloys of $Ge_{20}Se_{80-x}Ag_x$ (x = 0, 10, 15, 20) 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 dia. ∼8 mm) with a vacuum $\sim 10^{-5}$ torr. The ampoules containing the materials were heated to 1000 °C and held at that temperature for 10–12 hours. The temperature of the furnace was raised slowly at a rate ∼ 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 homogeneous glassy alloys. After rocking for about 10 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping 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. X-ray diffraction pattern for $Ge_{20}Se_{70}Ag_{10}$ alloy is given in Figure 1. XRD pattern for other composition were also of the same nature.

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 ∼0.12–0.27 mm) was used for the present measurements. The films were kept in deposition chamber in the dark for 24 hours before mounting them in the sample holder. This was done to alloy sufficient annealing at room temperature so that a metastable thermodynamic equilibrium may be attained in the samples as suggested by Abkowitz [28] 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 the 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 $\sim 10^{-2}$ torr was maintained throughout the measurements. A d.c. voltage (0 to 330 V) was applied across the sample and the resultant current was measured by a digital Pico-Ammeter. I-V characteristics were measured at various fixed temperatures (303–343 K) in these films. 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. Before measuring I-V characteristics, thin films were annealed in a vacuum $\sim 10^{-2}$ torr near glass transition temperature for two hrs in the same sample holder that was used for the above measurements.

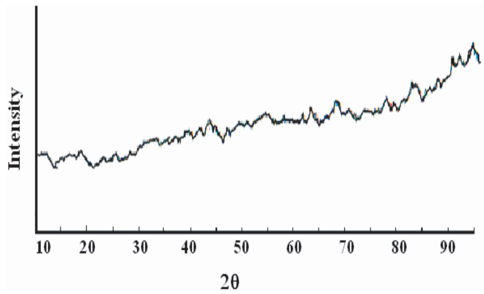

Fig. 1. X-ray diffraction pattern for $Ge_{20}Se_{70}Ag_{10}$ alloy.

3 Results and discussion

In the present work, I-V characteristics of thin films of $Ge_{20}Se_{80-x}Ag_x$ (x = 0, 10, 15, 20) are examined at various temperatures (303–343 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 localized states $g(E) = g_0$, the current (I) at a particular voltage (V) is given by the following relation [29]

$$I = (eA\mu n_0 V/d)\exp(SV) \quad (1)$$

where 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

$$S = 2\varepsilon_r\varepsilon_0/e\, g_0 k\, T\, d^2. \quad (2)$$

As evident from equations (1) and (2), in case of space charge limited conduction, 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 $Ge_{20}Se_{80-x}Ag_x$ (x = 0, 10, 15, 20) are plotted in Figure 2. The slope (S) of these curves decreases linearly with temperature for all the samples (see Fig. 3).

These results indicate the presence of space charge limited conduction in all the samples used. However, most thermally assisted conduction mechanisms display

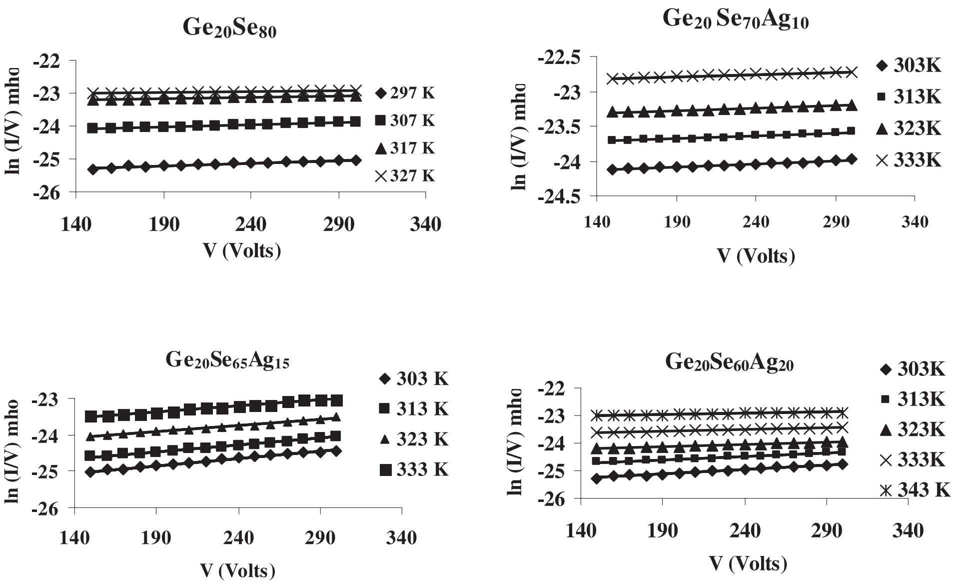

Fig. 2. ln I/V vs. V curves at different temperatures for a-$Ge_{20}Se_{80-x}Ag_x$ system.

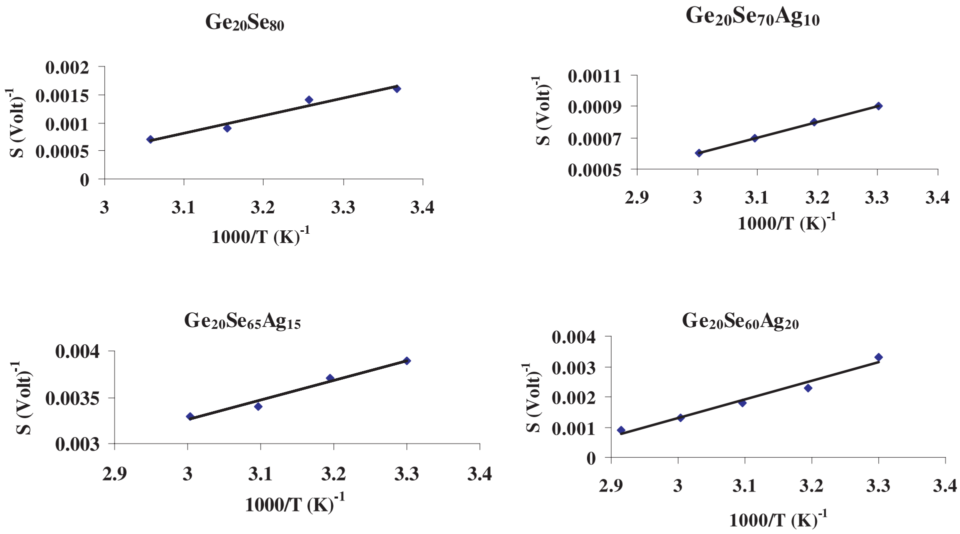

Fig. 3. Slope (S) vs. $1000/T$ curves for a-$Ge_{20}Se_{80-x}Ag_x$ system.

the similar behaviour. Therefore, we have performed the scaling property of SCLC as a function of the interelectrode spacing to discriminate SCLC against the thermally assisted conduction mechanisms. For SCLC mechanism, slope S is inversely proportional to d^2 according to equation (2). We have therefore measured I-V characteristics at room temperature (301 K) for all the samples having different electrode spacing. The values of the slopes (S) for different electrode spacing in case of $Ge_{20}Se_{80}$ are plotted against $1/d^2$ in Figure 4. Similar results were obtained in other samples. This confirms the validity of equation (2) and excludes the possibility of thermally assisted conduction mechanisms. Hence, the present measurements confirm the presence of SCLC in the present samples.

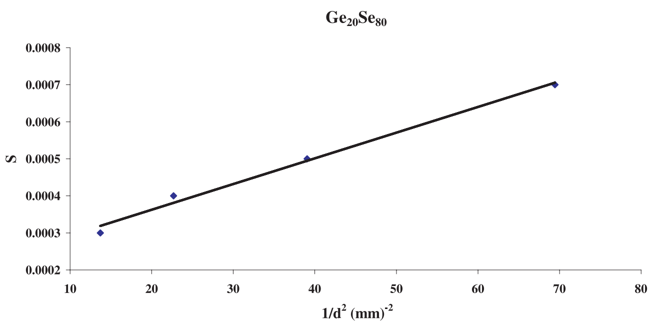

Fig. 4. Slope (S) vs. $1/d^2$ curve for $Ge_{20}Se_{80}$ alloy at a fixed temperature 301 K.

Thin films contain a large number of defects due to dangling bonds that give rise to large number of localised defect states. These localised states act as carrier trapping centers and after trapping the injected charge from

Table 1. Composition dependence of density of localized states (g_0) in a-$Ge_{20}Se_{80-x}Ag_x$ films.

Samples	Slope of S vs. $1000/T$ curve	ε_r (120 Hz, 303 K)	g_0 (density of localized states in eV^{-1} cm^{-3})
a-$Ge_{20}Se_{80}$	3.1×10^{-3}	15.0	4.3×10^{14}
a-$Ge_{20}Se_{70}Ag_{10}$	1.0×10^{-3}	15.0	1.33×10^{15}
a-$Ge_{20}Se_{65}Ag_{15}$	2.1×10^{-3}	15.0	6.35×10^{14}
a-$Ge_{20}Se_{60}Ag_{20}$	6.1×10^{-3}	15.0	2.18×10^{14}

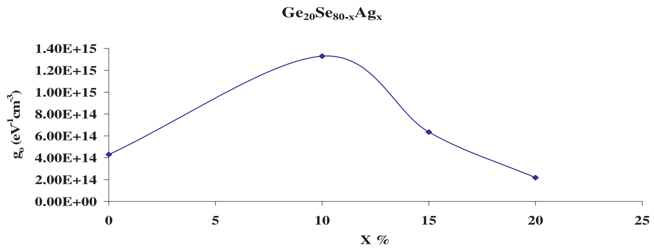

Fig. 5. Density of localized states (g_0) vs. Ag concentration in a-$Ge_{20}Se_{80-x}Ag_x$ system.

electrodes, they become charged and thereby expected to build up a space charge. This build up of space charge then play the key role in the determination of SCLC process.

Using equation (2), we have calculated the density of localised states from the slopes of Figure 2. 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 values of relative dielectric constant agree with reported by Fouad et al. [14]. The results of these calculations are given in Table 1 and plotted against Ag concentration in Figure 5. It is clear that on addition of Ag in Se-Ge alloy, density of localized states first increases till 10 at% of Ag and then decreases (Fig. 5). In our earlier photoconductive studies, similar results have been observed [15].

Many approaches have been proposed to explain the compositional dependence of various physical properties of chalcogenide glasses [30–33]. One of these approaches is a topological model, which are based on the constraint theory [31,32] and on the structural transitions considerations [33]. In these models, the properties can be discussed is terms of the average coordination number $\langle z \rangle$. In the constraint model [31,32], equating the number of operating constraints to the number of degrees of freedom, $\langle z \rangle$ of the most stable glass is shown to be 2.4. At this value of $\langle z \rangle$, the glass network changes from an elastically floppy (polymeric glass) type to a rigid (amorphous solid) type. By extension of the topological model to the medium ranged structures, other features at $\langle z \rangle = 2.67$ have also been observed [33]. However, the features observed at $\langle z \rangle = 2.67$ were attributed to a change from two-dimensional layered structure to a three-dimensional network arrangement due to cross-linking. In the present case a discontinuity in g_0 is observed at 10 at% of Ag showing a discontinuity at an average coordination number $\langle z \rangle = 2.60$, which is closer to the value in topological models described above.

4 Conclusions

I-V characteristics have been studied in amorphous thin films of $Ge_{20}Se_{80-x}Ag_x$ (x = 0, 10, 15, 20). At low fields ($<10^3$ V/cm), an ohmic behaviour is observed. However, at high fields ($\sim 10^4$ V/cm), a super ohmic behaviour is observed. The density of localized states near Fermi level is calculated by fitting the data to the theory of SCLC in case of uniform distribution of localised states. On addition of Ag in $Ge_{20}Se_{80}$ alloy, density of localized states first increases till 10 at% of Ag and then decreases. A discontinuity in g_0 is observed at 10 at% of Ag showing a discontinuity at an average coordination number $\langle z \rangle = 2.60$, which is closer to the value in the topological models.

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