Role of Cu additive in the density of localized states in \( a-\text{Ge}_{20}\text{Se}_{80} \) glassy alloy

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Received 5 December 2006; revised 19 June 2007; accepted 29 October 2007

The \( dc \) conductivity at high electric fields in vacuum evaporated amorphous thin films of \( \text{Ge}_{20}\text{Se}_{80} \) and \( (\text{Ge}_{20}\text{Se}_{80})_{98}\text{Cu}_{2} \) glassy alloys has been measured. Current-voltage (\( I-V \)) characteristics have been measured at various fixed temperatures. In these samples, ohmic behaviour is observed at low electric fields. However, at high electric fields (\( E\sim10^{4}\text{V/cm} \)), 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 has been calculated. An increase in DOS has been found when we incorporate Cu in the pure binary \( \text{Ge}_{20}\text{Se}_{80} \) glassy system. The peculiar role of Cu as a third element in the binary \( \text{Ge}_{20}\text{Se}_{80} \) glassy alloy is also discussed.

Keywords: Thin films, Chalcogenide glasses, Space charge limited conduction, Density of defect states

1 Introduction

Study of the electrical conduction of any medium gives us an in-sight into the transport mechanism of the prevailing charge carriers. In low-field conduction, the mobility and free carrier concentration are assumed to be constant with field. However, the application of a high field to a free carrier system may influence both the mobility and the number of charge carriers.

Thin films of chalcogenide glasses have been extensively studied during the past few years because of their potential applications. Stable glasses which have good photosensitive properties have been produced and can be doped \( n \) or \( p \) type. The effect of incorporation of third element in binary chalcogenide glassy alloys has always been an interesting problem in getting relatively stable glassy alloys as well as to change the conduction from \( p \) to \( n \) as most of these glasses show \( p \) type conduction only.

The coordination number of Ge is 4 and Se is 2, so at \( x = 20 \), the value of \( < r > = 2.4 \) in \( a-\text{Ge}_{x}\text{Se}_{100-x} \) system. What happens to the \( \text{Ge}_{20}\text{Se}_{80} \) system, when it is alloyed with a second element of group IV, is very important from the basic as well as application point of view. In Ge-Se and Se-In systems, some metallic additives have been found\(^1\)\(^-\)\(^6\) to change conduction from \( p \) type to \( n \) type and hence these binary systems are of great importance.

Cu doped chalcogenide glasses have also recently drawn great attention\(^7\)\(^-\)\(^8\) due to their own importance and as we know that the density of localized states (DOS) is the key parameter to predict the suitability of these glasses to use them in respective devices; therefore, the determination of DOS has been an important issue since the discovery of these glasses.

As high field effects are most readily observed in these materials because of their low conductivity (Joule heating is negligibly small at moderate temperatures) and have been studied by various groups working in this field\(^9\)\(^-\)\(^17\). The result of these researchers have been interpreted in terms of heating effect, space charge limited conduction (SCLC) and high field conduction due to the Poole-Frenkel effect. This indicates that the interpretation of the high field data is highly intriguing in these materials and much has to be done in this field.

The high field effects in the well known binary Ge-Se and ternary Ge-Se-Cu glassy alloy have been measured. Space charge limited conduction has been used as a tool to measure the DOS near Fermi level. Effect of Cu additive on DOS in pure binary Ge-Se is also discussed.

2 Experimental Details

Glassy alloys of \( \text{Ge}_{20}\text{Se}_{80} \) and \( (\text{Ge}_{20}\text{Se}_{80})_{98}\text{Cu}_{2} \) systems are prepared by quenching technique. High purity (99.999 %) materials are weighed according to their atomic percentages and are sealed in quartz ampoule (length ~ 5 cm and internal dia ~ 8 mm) with

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a vacuum ~ 1.3×10⁻³ Pa. The ampoule containing the materials are heated to 1000°C and held at that temperature for 10-12 h. The temperature of the furnace is raised slowly at a rate of 3–4°C/min. During heating, the ampoule is constantly rocked, by rotating a ceramic rod to which the ampoule is tucked away in the furnace. This is done to obtain homogeneous glassy alloy.

After rocking for about 10 h, the obtained melt is cooled rapidly by removing the ampoule from the furnace and dropping to ice-cooled water. The quenched sample of the glassy alloy is taken out by breaking the quartz ampoule. The amorphous nature of sample was confirmed by the absence of any sharp peak in the X-ray diffraction pattern. Compositional analysis was performed using electron probe microanalysis (EPMA) technique.

Thin film of these glasses has been prepared by vacuum evaporation technique keeping glass substrate at room temperature. Vacuum evaporated indium electrode at bottom was used for the electrical contact. The thickness of the film is ~ 500 nm. The co-planar structure (length ~ 1.2 cm and electrode separation ~ 0.12 mm) was used for the present measurements. A vacuum ~ 1.3 Pa was maintained in the entire temperature range 293–363K.

The thin films were kept in the deposition chamber in the dark for 24 h before mounting them in the sample holder. This is done to allow sufficient annealing at room temperature so that a metastable thermodynamic equilibrium may be attained in the samples as suggested by Abkowitz. Before measuring the dc conductivity, the films are first annealed at 370K for one hour in a vacuum ~ 1.3 Pa. I-V characteristics is found to be linear and symmetric up to 10 V. The present measurements are, however, made by applying a voltage up to 300 V across the films. The resulting current is measured by Keithley electrometer (Model No. 6517A). The heating rate is kept quite small (0.5 K/min) for these measurements. Thin film sample is mounted in a specially designed sample holder. A vacuum ~ 1.3 Pa is maintained throughout the measurements. The temperature of the film is controlled by mounting a heater inside the sample holder, and measured by a calibrated copper-constantan thermocouple mounted very near to the film.

3 Results and Discussion

Results of I-V characteristics at different temperature show that in the glassy sample studied here, ohmic behaviour is observed at low voltages, i.e., up to 10 V which is actually applied across the sample. However, at higher voltages (E ~ 10⁴ V/cm), a super-ohmic behaviour is observed in the samples. Here, ln I/V versus V curves are found to be straight lines. Figs1 and 2 show such curves in case of Ge₂₀Se₈₀ and (Ge₂₀Se₈₀)₉₈Cu₂ glassy alloys. According to the theory of SCLC, in the case of an uniform distribution of localized states having density $g_0$, the current (I) at a particular voltage (V) is given by:

$$I = (2e A \mu n_0 V / d) \left[ \exp \left( SV \right) \right] \cdots (1)$$

Where $e$ is the electronic charge, $A$ the cross-sectional area of the film, $n_0$ the density of free charge carriers, $d$ the electrode spacing and $S$ is given by:

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

where $\varepsilon_r$ is the static value of the dielectric constant, $\varepsilon_0$ the permittivity of free space, $g_0$ the density of traps near the Fermi level and $k$ is Boltzmann's constant.

![Fig. 1—Plots of ln I/V versus V curve for α-Ge₂₀Se₈₀ at different temperatures](image1)

![Fig. 2—Plots of ln I/V versus V curve for α- (Ge₂₀Se₈₀)₉₈Cu₂ at different temperatures](image2)
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.

According to Eq. (1), ln $I/V$ versus $V$ curves should be straight lines whose slope should decrease with increase in temperature as evident from Eq. (2). It is clear from Figs 1 and 2 that the slope ($S$) of ln $I/V$ versus $V$ curves is not the same at all the measuring temperatures. The value of these slopes is plotted as a function of temperature in Fig. 3 for the glassy system used in the present study. The slope decreases linearly with the increase in temperature (Fig. 3). These results indicate the presence of SCLC in the present samples.

Using Eq. (2), we have calculated the density of localized states from the slope of Fig. 3. The value of the relative dielectric constant $\varepsilon_r$ is measured by using capacitance measuring assembly model G R 1620 A P, employing the three terminal techniques. The results of these calculations are presented in Table 1. It is observed that if we compare Ge-Se with (Ge-Se)$_{98}$Cu$_2$, the presence of covalent character in the latter case is more than that of the first system with the result the possibility of higher $\varepsilon_r$ in the latter case than that of the first one . The results show that the density of defect states near mid-gap is substantially affected by the addition of a third element to the binary Ge-Se glassy alloy. Since 2 at. % of Cu additive is incorporated in Ge-Se system; these atoms cannot be considered as impurities only. The properties of such ternary materials must, therefore, be attributed to the modifications in structure of the host alloy on the addition of a third element.

According to Phillips, Ge-Se alloys must be considered as small chemically ordered clusters embedded in a continuous network. Some of these clusters may be (Se)$_n$ chains, Ge(Se$_{1/2}$)$_4$ corner-sharing tetrahedral or Ge(Se$_{1/2}$)$_6$ ethane-like structural units. The first two types of clusters may be predominant in Se-rich alloys (as in the present case). The addition of Cu may modifies the Ge(Se$_{1/2}$)$_4$ clusters, penetrating into them to form units containing all three elements, Ge, Cu and Se, as suggested by Pazin et al. in the case of Bi in Ge-Se glassy alloys.

Incorporation of third element Cu to Ge-Se binary alloy is expected to modify the structure of the host alloy, with the new element entering into chemical bond formation with Ge and/or Se as reported by Shukla et al., in their X-ray K-absorption studies in Ge-Se-M (M=Ag, In, Pb and Cd) glassy alloys.

While studying the effect of chlorine on electro-photographic properties of Se-Te, Onozuka et al., observed that the increase in residual potential caused by Te addition to Se is counteracted by the addition of chlorine to Se-Te glassy alloy. The results were interpreted on the basis of a structural defect model where Te was assumed to form positively charged impurities due to small electron affinity of Te as compared to Se while chlorine atoms having larger electron affinity formed negatively charged impurities, thereby compensating the effect of Te.

Along the same lines, one can expect that when a third element Cu having lower electron-negativity than Se is added into Ge-Se glassy alloys, positively charged defects will be created, thus, increasing the density of defect states in ternary Ge-Se-Cu system as compared to pure binary Ge-Se glassy alloy.

Our SCLC data also confirm that the density of defect states is increasing with incorporation of Cu in pure binary Ge$_{20}$Se$_{80}$ glassy system.

4 Conclusions

$I$-$V$ characteristics have been studied in amorphous thin films of Ge$_{20}$Se$_{80}$ and (Ge$_{20}$Se$_{80})_{98}$Cu$_2$ glassy

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**Table 1—Density of localized states ($g_0$) in Ge$_{20}$Se$_{80}$ and (Ge$_{20}$Se$_{80})_{98}$Cu$_2$ glassy system**

<table>
<thead>
<tr>
<th>Glassy alloys</th>
<th>Slope of S versus $1000/T$ curves</th>
<th>$\varepsilon_r$ (at 120 Hz, 305 K)</th>
<th>$g_0$ (eV$^{-1}$cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{20}$Se$</em>{80}$</td>
<td>8.3 x 10$^{-3}$</td>
<td>2.62</td>
<td>2.82 x 10$^{13}$</td>
</tr>
<tr>
<td>(Ge$<em>{20}$Se$</em>{80})_{98}$Cu$_2$</td>
<td>2.3 x 10$^{-3}$</td>
<td>4.89</td>
<td>1.93 x 10$^{14}$</td>
</tr>
</tbody>
</table>

Fig. 3—Plots of $S$ versus $1000/T$ curve for Ge$_{20}$Se$_{80}$ and (Ge$_{20}$Se$_{80})_{98}$Cu$_2$ glassy system
system. At low fields, ohmic behaviour is observed. However, at higher fields (~$10^4$ V/cm) super ohmic behaviour 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 near Fermi-level is calculated. It is found that the density of defect states is increasing with incorporation of Cu in pure binary Ge$_{20}$Se$_{80}$ glassy system. This increase in DOS has been explained with the electro-negativity difference between the constituent elements used in making the above glassy system.

Acknowledgement
S Kumar is grateful to University Grants Commission, New Delhi, for providing a major research project during the course of this work.

References