

Role of Sn in the Density of Defect States in a-Se_{0.75}Te_{0.25} and a-Se_{0.85}Te_{0.15}Thin Films*

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Abstract

In this paper we report the effect of Sn incorporation in the density of defect states of two binary Se-Te glassy systems, comparing the properties of a-Se_{0.75}Te_{0.25}, a-Se_{0.85}Te_{0.15} and a-Se_{0.75}Te_{0.15}Sn_{0.10} glassy alloys. Properties of d.c. conductivity at high electric fields in vacuum were examined; and current-voltage (I-V) characteristics have been measured at various fixed temperatures. Ohmic behavior is observed at low electric fields; while at high electric fields ($E \sim 10^4$ V/cm), non-ohmic behavior is observed. An analysis of the experimental data confirms the presence of space charge limited conduction (SCLC) in the studied glassy materials. Density of defect states (DOS) near Fermi level is calculated by fitting data to SCLC theory. The peculiar role of the third element Tin, as an impurity in the pure binary Se_{0.75}Te_{0.25} and Se_{0.85}Te_{0.15} glassy alloys, is also discussed in terms of electro-negativity difference.

Key Words: Thin films, Chalcogenide glasses, SCLC, DOS.

1. Introduction

Amorphous semiconductors, in particular Se-Te alloys, have gained much importance among chalcogenide glasses due to their higher photosensitivity, greater hardness, higher crystallization temperature and smaller aging effects compared to pure selenium glass. Because of these advantages, these alloys are nowadays preferred in various solid state devices. Sn doped chalcogenide glasses [1–5] have recently drawn much attention due to their applications in various solid state devices. Thus there is need to predict the suitability of various glass compositions, with the density of localized states (DOS) being a key parameter.

Se-Te alloys have a higher photosensitivity than pure Se. These alloys are also harder than pure Se and are therefore widely used and preferred to pure Se [1]. The properties of chalcogenide glassy semiconductors are usually affected by the addition of impurities as third element. 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. In Ge-Se and Se-In systems, some metallic additives have been found [6–11] to change conduction from p type to n type and hence these binary systems are of great importance.

The effect of incorporation of some metallic impurity in Se-Te binary glassy system have been studied by various workers working in this field [12–14] and their results have been interpreted in terms of change in the

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density of localized states near Fermi level. As for example, during photoconductivity measurements Mehra et. al., [12] have reported the creation of some new defect states with Sb contents in Se-Te binary glassy alloys. Arora et. al., [13] have found defect states dependence of dielectric properties when third element (Cd, In and Sb) as an impurity is being added in $\text{Se}_{80}\text{Te}_{20}$ glassy alloy. Similar kind of behavior has also been reported by Goel et. al., [14] during their dielectric relaxation measurements in glassy $\text{Se}_{80-x}\text{Te}_{20}\text{Ge}_x$ alloy. Direct measurements of the DOS in the aforesaid glassy system have not been reported so far. As high field effects are also 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 [15–22]. The result of these workers 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. In our earlier measurements [23] we have reported the effect of Ge and Sb as an impurity on the density of defect states in pure binary Se-Te system. We have used SCLC as a tool for measuring the DOS in Se-Te, Se-Te-Ge and Se-Te-Sb glassy networks, and found that the role of germanium and antimony impurities was very interesting and entirely different. In the case of Sb, an increase in DOS was observed while a decrease was found when Ge was incorporated as a third element in binary Se-Te glassy system. The change in DOS on impurity incorporation was explained in terms of the change in structure of these glasses.

In view of the above we have decided to study the effect of Sn as an impurity in the two well-known binary systems a- $\text{Se}_{0.75}\text{Te}_{0.25}$ and a- $\text{Se}_{0.85}\text{Te}_{0.15}$. The present paper therefore reports the effect of incorporation of Sn in the density of defect states by studying their non-ohmic behavior at high fields.

The next section describes the experimental details of the measurements. The results are presented and discussed in the third section. The final section deals with the conclusions drawn from the present work.

2. Experimental

Glassy alloys of a- $\text{Se}_{0.75}\text{Te}_{0.25}$, $\text{Se}_{0.85}\text{Te}_{0.15}$ and $\text{Se}_{0.75}\text{Te}_{0.15}\text{Sn}_{0.10}$ are prepared by quenching technique. High purity (99.999 %) materials are weighed according to their atomic (molar) fractions and were sealed in quartz ampoules (of length ~ 5 cm and internal diameter ~ 8 mm) with a vacuum $\sim 1.3 \times 10^{-3}$ Pa. The ampoules containing the materials were heated to 1000°C and held at that temperature for 10–12 hours. Furnace temperature was raised slowly at a rate of $3\text{--}4^\circ\text{C}/\text{min}$. During heating, all ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules are attached in the furnace. This is done to obtain homogenous glassy alloys.

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

Thin films of these glasses are prepared by vacuum evaporation technique, keeping glass substrates at room temperature. Vacuum evaporated indium electrodes placed at the bottom are used for electrical contact. Thickness of the films is ~ 500 nm. The co-planar structure (length ~ 1.2 cm and electrode separation ~ 0.12 mm) are used for the present measurements. A vacuum of ~ 1.3 Pa is maintained over the entire temperature range (295 K to 335 K).

The films are kept in the deposition chamber in the dark for 24 hours 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 [24]. Before measuring the d.c. conductivity, the films are first annealed at 340 K for one hour in a vacuum of ~ 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 a digital Pico-Ammeter. The

heating rate is kept quite small (0.5 K/min) for these measurements. Thin films samples are mounted in a specially designed sample holder. The temperature of the films is controlled by mounting a heater inside the sample holder, and measured by a calibrated copper-constantan thermocouple mounted very near to the films.

3. Results and Discussion

Results of I-V measurements at different temperature shows that in all samples studied here, ohmic behavior is observed at low voltages. However, at higher voltages ($E \sim 10^4$ V/cm), a super-ohmic behavior is observed in all the samples. Since planar geometry of thin films has been used in the present measurement therefore electric field may be supposed to be uniform throughout the sample. Figure 1 shows such curve for the three samples studied here at room temperature (295 K). In Figures 2–4 plots of $\ln(I/V)$ as a function of voltage for, respectively, glasses a- $\text{Se}_{0.75}\text{Te}_{0.25}$, $\text{Se}_{0.85}\text{Te}_{0.15}$ and $\text{Se}_{0.75}\text{Te}_{0.15}\text{Sn}_{0.10}$ at different temperatures. And, indeed, we see all plots are essentially linear, and further, show clear super-ohmic behavior. According to SCLC theory, in the case of a uniform distribution of localized states having density g_o , the current I at a particular voltage V is given by [25]

$$I = (2eA\mu n_o V/d) \exp(SV), \quad (1)$$

where, e is the charge of the electron, A is the cross sectional area of the film, n_o is the density of free charge carriers, d is the electrode spacing and S is given by the relation

$$S = e\varepsilon_r\varepsilon_o/eg_0kTd^2. \quad (2)$$

Here, 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 Boltzmann's constant.

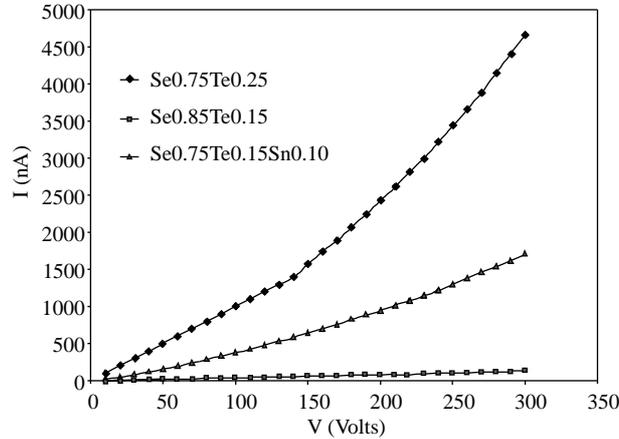


Figure 1. Plots of I-V characteristics for the three samples at room temperature (295 K).

It should be noted that equation 1 is not an exact solution of the SCLC relation, 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 equation 1, $\ln(I/V)$ should linear as a function of V , and whose slope should decrease with increase in temperature, as evident from equation 2. It is clear from Figures 2–4 that the slope S of $f(V) = \ln(I/V)$ is not the same at all temperatures where measurements were conducted. The value of these

slopes is plotted as a function of reciprocal temperature in Figure 5 for the three glassy systems used in the present study. It is clear from this figure that the slope decreases linearly with increase in temperature. These results indicate the presence of SCLC in the present samples.

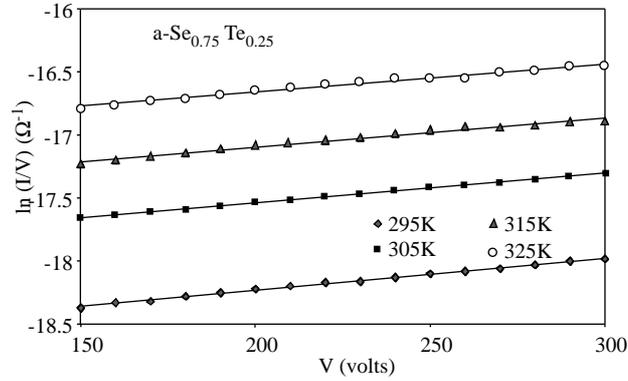


Figure 2. Plots of $\ln(I/V)$ as a function of V for $a\text{-Se}_{0.75}\text{Te}_{0.25}$ at different temperatures.

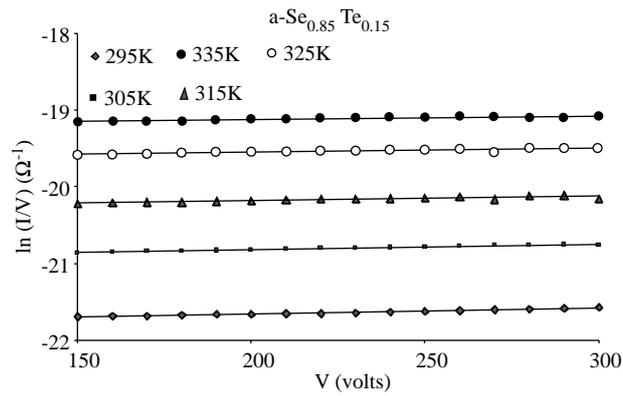


Figure 3. Plots of $\ln(I/V)$ as a function of V for $a\text{-Se}_{0.85}\text{Te}_{0.15}$ at different temperatures.

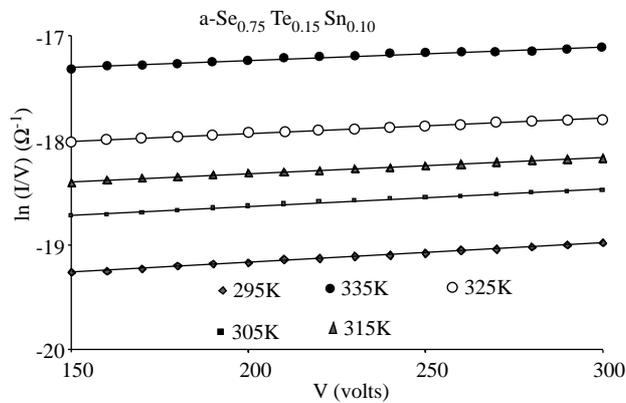


Figure 4. Plots of $\ln(I/V)$ as a function of V for $a\text{-Se}_{0.75}\text{Te}_{0.15}\text{Sn}_{0.10}$ at different temperatures.

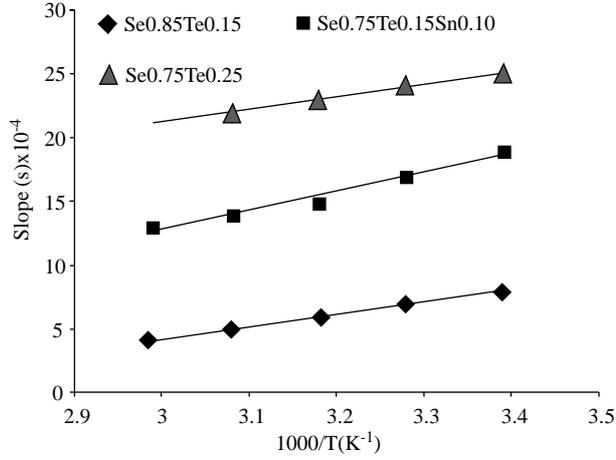


Figure 5. Plots of S as a function of $1000/T$ for a- $\text{Se}_{0.75}\text{Te}_{0.25}$, $\text{Se}_{0.85}\text{Te}_{0.15}$ and $\text{Se}_{0.75}\text{Te}_{0.15}\text{Sn}_{0.10}$ glassy systems.

Thin films contain a large number of defects due to dangling bonds that give rise to large number of localized defect states. These localized 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 play the key role in the determination of SCLC process.

Using equation 2, we have calculated the density of localized states from the slope of Figure 5. The value of the relative dielectric constant ϵ_r is measured by using capacitance measuring assembly model GR 1620 AP, employing the three terminal techniques. The results of these calculations are given in Table 1. It is clear from this table that the addition of the third element Sn decreases the DOS in the pure Se-Te glassy network. However, this decrease is less in $\text{Se}_{0.85}\text{Te}_{0.15}$ than in $\text{Se}_{0.75}\text{Te}_{0.25}$, which could be explained as follows.

Table 1. Density of localized states in the three glassy systems under study.

Glassy Alloys	Slope of S vs. $10^3/T$	ϵ_r (120 Hz, 303 K)	g_o ($\text{eV}^{-1}\text{cm}^{-3}$)
$\text{Se}_{0.85}\text{Te}_{0.15}$	9.99×10^{-4}	7.78	6.93×10^{14}
$\text{Se}_{0.75}\text{Te}_{0.15}\text{Sn}_{0.10}$	1.51×10^{-3}	3.97	2.34×10^{14}
$\text{Se}_{0.75}\text{Te}_{0.25}$	9.70×10^{-4}	18.38	1.69×10^{15}

When isoelectronic atom Te is added to amorphous Selenium, the density of defect states is increased and hence the residual potential increases in xerographic experiment. Onozuka et al [26] 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 electro-negativity of Te as compared to Se [27], while Cl atoms having higher electro-negativity than Selenium [27] form negatively charged impurities, thereby compensating the effect of Te [26].

Along the same lines, one can expect that when Sn, having lower electro-negativity than Se and Te [27], is introduced in $\text{Se}_{0.85}\text{Te}_{0.15}$, positively charged defects will be created, but the extent of their creation will be smaller since the amount of Te is same in both. On the other hand, when the same Sn is incorporated in $\text{Se}_{0.75}\text{Te}_{0.25}$, the DOS may decrease more sharply due to decrease in percentage of Te atom in $\text{Se}_{0.75}\text{Te}_{0.15}\text{Sn}_{0.10}$ than $\text{Se}_{0.75}\text{Te}_{0.25}$ binary glassy system as it is observed by us in our present measurements.

4. Conclusion

I-V characteristics have been studied in amorphous thin films of $\text{Se}_{0.75}\text{Te}_{0.25}$, $\text{Se}_{0.85}\text{Te}_{0.15}$ and $\text{Se}_{0.75}\text{Te}_{0.15}\text{Sn}_{0.10}$ glassy systems. At low fields, ohmic behavior is observed. However, at higher fields ($\sim 10^4$ V/cm) superohmic behavior is observed.

Analysis of the observed data shows the existence of SCLC in all 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 clear from the results obtained that the addition of Sn decreases the DOS in the pure Se-Te glassy network. The difference in order of decrease in DOS in the two $\text{Se}_{0.75}\text{Te}_{0.25}$ and $\text{Se}_{0.85}\text{Te}_{0.15}$ binary glassy system could be explained on the basis of the electro-negativity difference between the constituent elements used in making the above glassy alloys.

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