JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 4, August 2006, p. 1345 - 1348

Determination of the density of localized states in $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ glassy alloy

R. SINGH[a], S. K. TRIPATHI[b], S. KUMAR[a*]
[a] *Department of Physics, Christ Church College, Kanpur-208001, India*
[b] *Centre of Advanced study in physics, Panjab University, Chandigarh-160014, India*

The present paper reports the d. c. conductivity measurements at high electric fields in vacuum evaporated thin films of $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$glassy alloy. Current-Voltage (I-V) Characteristics have been measured at various fixed temperatures. In this sample, at low electric fields, ohmic behavior is observed. However, at high electric fields ($E\sim10^4$V/cm), non ohmic behavior is observed. An analysis of the experimental data confirms the presence of space charge limited conduction (SCLC) in the glassy material 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. The role of Sn as an impurity element in binary $Ge_{20}Se_{80}$ glassy alloy is also discussed.

(Received June 8, 2006; accepted July 20, 2006)

Keywords: Thin films, Chalcogenide glasses, Ge-Se-Sn, Space charge limited conduction, Density of localized states

1. Introduction

Because of their potential applications, thin films of chalcogenide glasses have been extensively studied during the past few years. Attempts have been made to produce stable glasses which have good photosensitive properties 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. 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.

Recently, there were investigated the effect of Bi on the electrical properties of germanium selenide [7] as well as the effect of Sn on optical parameters of a-$Ge_{20}Se_{80}$ [8]. The irradiation effect on the optical properties of Ag doped GeSe films has been investigated in [9].

The coordination number of Ge is 4 and Se is 2, so at x = 20, the value of < r > = 2.4 in a-Ge_xSe_{100-x} system. What happens to the $Ge_{20}Se_{80}$ 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. Sn belongs to the IV group and its atomic radii (1.41 Å) is more than that of Ge (1.22 Å). Bond-stretching forces acting as constraints are present in Ge, Se and Sn. These bond bending constraints are important in Ge and Se but may be ignored in Sn because the corresponding spring constant is weak compared to Ge and Se. This fact makes Ge-Se-Sn, a useful system to study as the addition of Sn is expected to reduce the number of constraints per atom [10]. A lot of studies have been done on Ge-Sn-Se system at higher concentration of Ge (≥ 33) [10,11], but not much work has been done at lower concentrations of Ge (≤ 30).

Sn doped chalcogenide glasses [12,13] have recently drawn great attention due to their applications in various solid state devices 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 a 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 [14-22]. 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.

It is interesting to note that SCLC for a uniform distribution of traps as well as the high-field conduction theories mentioned above lead to a similar kind of field dependence of the conductivity at different temperatures. To distinguish between these two processes, the measurements on samples having different electrode gaps are necessary. Therefore, we have measured the high field conduction at different temperatures on vacuum evaporated thin film of glassy $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ alloy having different electrode separation. The dependence of DC conductivity on the electrode separation confirms the presence of SCLC in the present samples. Using the theory of SCLC for the case of uniform distribution of traps, the density of localized states near the Fermi level is calculated for the sample used in the present study.

In our earlier measurements we have reported dielectric relaxation [23] in the present system and measurements of DOS in the pure binary Ge-Se glassy system had been reported by us in the past [24]. In this paper we report determination of DOS in Ge-Se-Sn ternary glassy system.

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 alloy of $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ system 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 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 hours. 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 homogenous glassy alloy.

After rocking for about 10 hours, 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 micro- analysis (EPMA) technique.

Thin film of the glass is prepared by vacuum evaporation technique keeping glass substrate at room temperature. Vacuum evaporated indium electrode at bottom is 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 –0.37 mm) is used for the present measurements. A vacuum ~ 1.3 Pa is maintained in the entire temperature range (305 K to 365 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 [25]. Before measuring the d. c. conductivity, the films are first annealed at 370 K for one hour in a vacuum ~ 1.3 Pa. I-V characteristics are found to be linear and symmetric up to 10 V. The present measurements are, however, made by applying a voltage upto 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 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 shows that in the glassy sample studied here, ohmic behavior is observed at low voltages, i.e., up to 100 V. However, at higher voltages (E ~ 10^4 V/cm), a super-ohmic behavior is observed in the sample. Here, ln I/V vs. V curves are found to be straight lines. Fig. 1 show such curves in case of $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$glassy alloy. 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 [23]:

$$I = (2\ e\ A\ \mu\ n_0\ V/\ d)\quad [\exp (SV)] \tag{1}$$

Here, e is the electronic charge, A is the cross sectional area of the film, n_o is the density of free charge carriers, d is the electrode spacing and S is given by:

$$S = 2\ \varepsilon_r\ \varepsilon_0\ /\ e\ g_0\ k\ T\ d^2 \tag{2}$$

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 Boltzmann's constant.

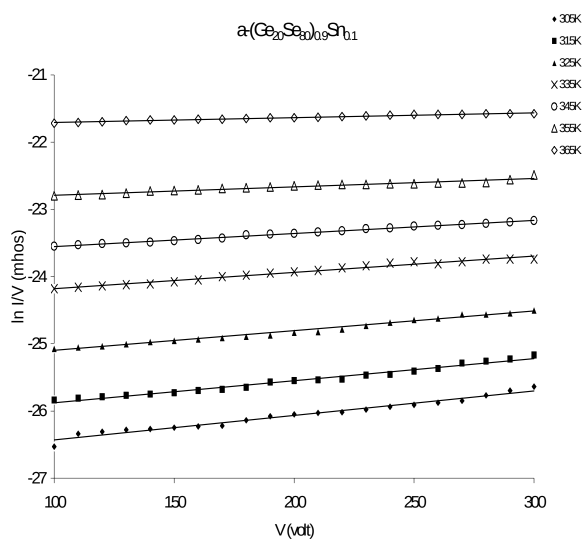

Fig. 1. Plots of ln I/V vs. V curve for a- $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ at different temperatures.

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.

According to eq. 1, ln I/V vs. V curves should be straight lines whose slope should decrease with increase in temperature as evident from eq. 2. It is clear from Fig. 1 that the slope (S) of ln I/V vs. 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. 2 for the glassy system used in the present study. It is clear from this figure that the slope decreases linearly with the increase in temperature. These results indicate the presence of SCLC in the present sample.

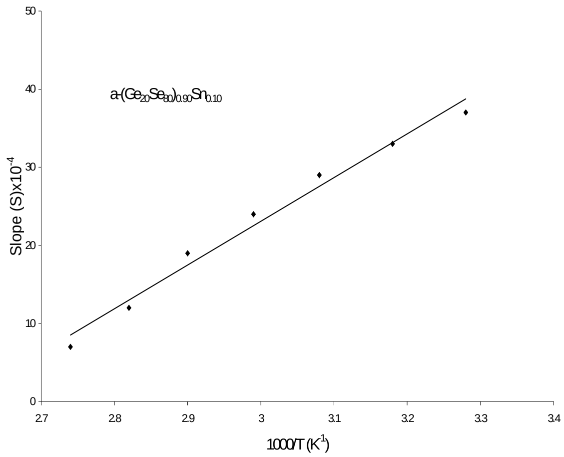

Fig. 2. Plots of S vs. 1000/T curve for $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ glassy system.

It may be mentioned here that nearly linear plots of ln I/V vs. V as well as a linear decrease of S with temperature can also be 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. However, in the case of field dependent conductivity, the plot of ln I/V vs. V must be independent of the electrode spacing ‘d’. On the other hand for any SCLC mechanism, the same plot gives different curves for different values of ‘d’. We have therefore measured I-V characteristics at room temperature (305 K) for samples having different electrode spacing. The results are plotted in Fig. 3. It is clear from this figure that different slopes are obtained at different electrode spacing. The values of these slopes are given in Table 1 and are plotted against $1/d^2$ in Fig. 4. This confirms the validity of eqn. (2) in the present case and excludes the possibility of any other high-field conduction processes mentioned above. Hence these measurements confirm the presence of SCLC in the present sample.

Table 1. Values of slopes of ln I/V vs. V curves for different electrode gaps in $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ glassy system.

Electrode gap (d) in mm	$1/d^2$(in mm^{-2})	Slopes (s) of ln I/V vs. V at T_{room} (305 K)
0.12	69.44	3.7×10^{-3}
0.19	27.70	1.4×10^{-3}
0.30	11.11	6.0×10^{-4}
0.37	7.31	4.0×10^{-4}

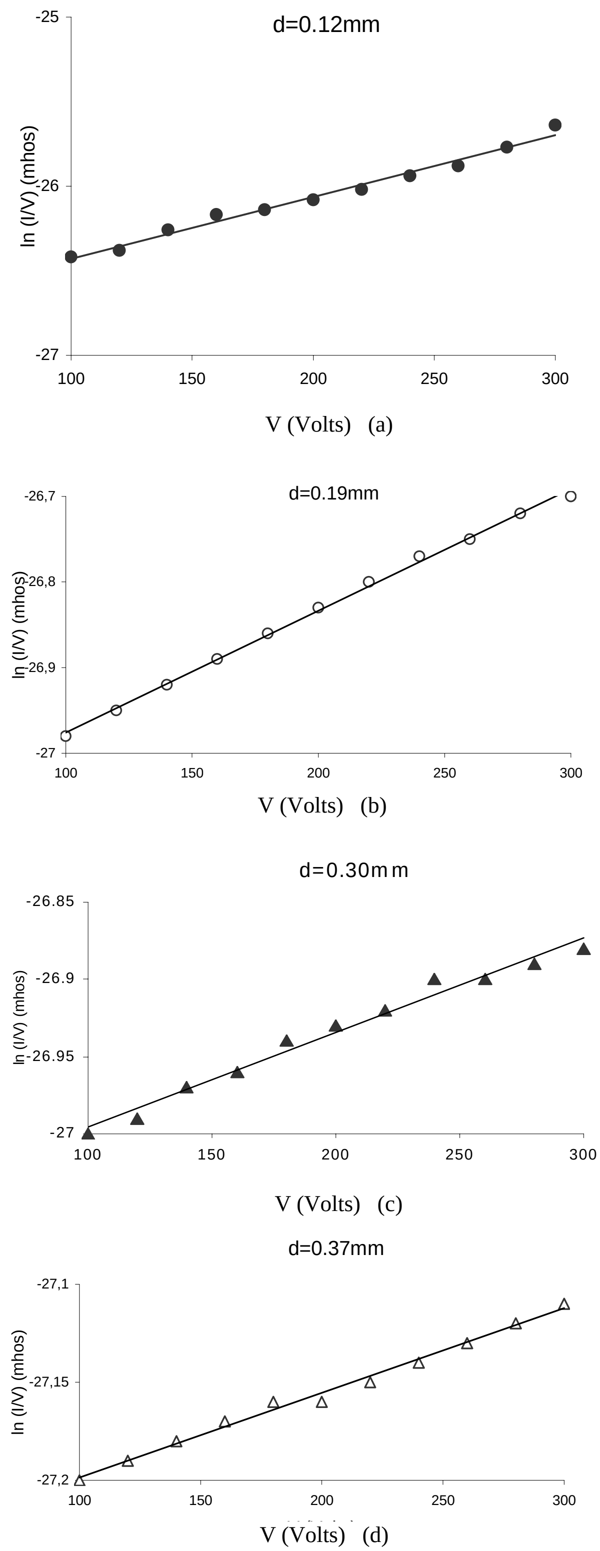

Fig. 3. Plots of ln I/V vs. V curve at room temperature having different electrode gaps for $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ glassy system.

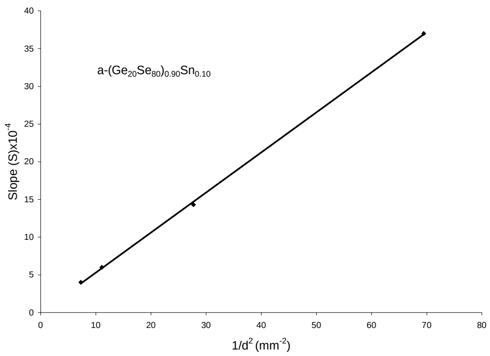

Fig. 4. S vs. $1/d^2$ curve for different electrode gaps for $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ glassy system.

Using eqn. 2, we have calculated the density of localized states from the slope of Fig. 2. The value of the relative dielectric constant ε_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 given in Table 2.

Table 2. Electrical parameters for density of localized states in $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ glassy alloy.

Temp. (K)	1000/T (K^{-1})	Slope of lnI/V vs V Curves
305	3.28	3.7×10^{-3}
315	3.18	3.3×10^{-3}
325	3.08	2.9×10^{-3}
335	2.99	2.4×10^{-3}
345	2.90	1.9×10^{-3}
355	2.82	1.2×10^{-3}
365	2.74	0.7×10^{-3}

Slope of S vs 1000/T curve	ε_r	g_o ($eV^{-1}cm^{-3}$)
5.6×10^{-3}	6.24	9.92×10^{13}

In our earlier measurements [27], we have shown that in these materials the Fermi level is not pinned and can be shifted quite significantly due to current injection by the application of electric field. Therefore, the value of DOS as reported above near the Fermi level is acceptable.

4. Conclusion

I-V characteristics have been studied in amorphous thin film of glassy $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ system. 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 sample 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. The role of Sn as an impurity element in binary $Ge_{20}Se_{80}$ glassy alloy was also discussed.

Acknowledgements

The work was suportted by University Grant Comission, New Delhi, India.

S. Kumar is grateful to U.G.C., New Delhi for providing a major research project during the course of this work.

References

[1] N. Tohge, T. Minami, M. Tanaka, J. Non-Cryst. Solids **37**, 23 (1980).
[2] P. Nagel, H. Ticha, L. Tichy, A. Triska, J. Non-Cryst. Solids **59**, 1015 (1983).
[3] N. Tohge, M. Hideaki, T. Minami, J. Non-Cryst. Solids **95**, 809 (1987).
[4] K. L. Bhatia, G. Parthasarathy E. S. R. Gopal, A. K. Sharma. Solid State Commun. **51**, 739 (1984).
[5] K. L. Bhatia, G. Parthasarathy, D. P. Gosan, E. S. R. Gopal Phil.Mag **B51,** L63 (1985).
[6] S. Kohli, V. K. Sachdev, R. M. Mehra, P. C. Mathur, Phys. Stat. Sol. B **209**, 389 (1998).
[7] G. Singh, J. Sharma, A. Thakur, N. Goyal, G. S. S. Saini, S. K. Tripathi, J. Optoelectron. Adv. Mater. **7**(4), 2069 (2005).
[8] A. Thakur, V. Sharma, G. S. S. Saini, N. Goyal, S. K. Tripathi, J. Optoelecton. Adv. Mater. **7**(4), 2077 (2005).
[9] S. K. Tripathi, A. Thakur, G. Singh, J. Sharma, K. P. Singh, G. S. S. Saini, N. Goyal, J. Optoelectron. Adv. Mater. 7(4), 2095 (2005).
[10] S. A. Fayek, Infrared physics & technology **46**, 193 (2005).
[11] H. Tichá, L. Tichý, P. Nagels, E. Sleeckx, R. Callaerts, J. Phys. & Chem. Solids **61**, 545 (2000).
[12] P. Boolchand, W. J. Bresser, K. L. Chopra, Bull Am Phys Soc **44**, 1434 (1999).
[13] P. Boolchand, W. J. Bresser, Philos Mag B **80**, 1757 (2000).
[14] P. S. Nikam, H. S. Aher, Ind. J. Pure and Appl. Phys. **34**, 393 (1996).
[15] S. Abou El-Hassan, Physica B. **307**, 86 (2001).
[16] S. M. El-Sayed, Vacuum **65**, 177 (2002).
[17] K. Yilmaz, M. Parlak, C. Ercelebi, J. Mat. Sci.: Materials in Electronics. **15**(4), 225 (2004).
[18] A. Kumar, S. Kumar, R. Arora, Solid State Commun. **78**, 651 (1991).
[19] S. Kumar, R. Arora, A. Kumar, J. Mater. Sci. Lett **10**, 1280 (1991).
[20] S. Kumar, R. Arora, A. Kumar, Solid State Commun 82, 725 (1992).
[21] S. Kumar, R. Arora, A. Kumar, Physica B **183,** 172 (1993).
[22] S. P. Singh, S. Kumar, A. Kumar, Vacuum **75**, 313 (2004).
[23] P. S. Chandel, A. Thakur V. Sharma, N. Goyal, S. K. Tripathi Ind. J of Pure & Appl. Phys. **42**, 539 (2004).
[24] A. Kumar, S. Kumar, R. Arora, Solid State Commun. **78**, 651 (1991).
[25] M. Abkowitz, Polymer Eng. Sci **24,** 1149 (1984).
[26] M. A. Lampert, P. Mark, Current Injection in Solids. New York: Academic Press, 1970.
[27] D. Kumar, S. Kumar, Japanese J. of Appl. Phys. **43**, 901 (2004).

*Corresponding author: dr_santosh_kr@yahoo.com

JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 4, August 2006, p. 1345 - 1348