Journal of Ovonic Research Vol. 4, No. 5, October 2008, p. 96 - 99

A COMPARATIVE STUDY OF LOCALIZED STATES IN Pb AND Ag DOPED Ge-Se GLASSY ALLOYS

V. S. Kushwaha, S. K. Dwivedi, A. Kumar[a*]
Dept. of Physics, Kanpur Institute of Technology, Kanpur, India
[a]Dept. of Physics, Harcourt Butler Technological Institute, Kanpur, India

The present paper reports the comparative analysis of localized defect states in glassy $Ge_{20}Se_{80-x}Ag_x$ (x = 0, 10, 15, 20) and $(Ge_{20}Se_{80})_{100-x}Pb_x$ (x = 0, 2, 4, 6) systems. The density of defect states is determined by space charge limited conduction measurements. It is observed that in glassy $Ge_{20}Se_{80-x}Ag_x$ the density of defect states increases with the concentration of Ag, becomes maximum and then decreases with Ag concentration. On the other hand, in glassy $(Ge_{20}Se_{80})_{100-x}Pb_x$, the density of defect states decreases with the concentration of Pb, becomes minimum and then increases with Pb concentration.

(Received August 25, 2008; accepted August 30, 2008)

Keywords: Amorphous Materials, Thin Films, Electronic Properties.

1. Introduction

Chalcogenide glasses are an important class of glassy materials as they behave as semiconductor and hence can be used for semiconducting devices similar to crystalline ones. However, it is found experimentally that it is difficult to have efficient doping (n type or p type) in these materials due to large density of defect states in the band gap.

Though, all chalcogenide glasses could not be doped, the properties of chalcogenide glassy semiconductors are usually affected by the addition of impurities when third element is added to the binary alloys. 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. Several physical properties are found to be improved by the addition of certain impurities.

Only those glass compositions can be used for photoconductive and photovoltaic devices, which have relatively smaller density of defect states. Therefore, a search of new materials is still continued which have lesser and lesser density of structural defect states. The measurement of such defect states is also difficult in these materials because of large density of defects and insufficient knowledge of electronic structure of these materials. To measure such defect states, different methods have been used with all their advantages and their limitations. One of the most direct methods for the determination of defect states involves the measurements of space charge limited conduction. In these materials, the density of defect states reported by different groups [4-7].

In our previous work [8, 9], the density of defect states is determined by using the theory of space charge limited conduction in glassy alloys of $Ge_{20}Se_{80-x}Ag_x$ (x = 0, 10, 15, 20) and $(Ge_{20}Se_{80})_{100-x}Pb_x$ (x = 0, 2, 4, 6). The aim of present paper is to report the comparative study of

*Corresponding author: dr_ashok_kumar@yahoo.com

localized defect states in these glassy systems as they show quite different composition dependence in these systems.

2. Experimental

Glassy alloys of $Ge_{20}Se_{80-x}Ag_x$ (x = 0, 10, 15, 20) and $(Ge_{20}Se_{80})_{100-x}Pb_x$ (x = 0, 2, 4, 6) are prepared by quenching technique. High purity (99.999 %) materials are weighed according to their atomic percentages. The actual amount of the constituent elements taken, for the preparation of glassy alloys. The materials are then sealed in quartz ampoules (length ~ 5 cm and internal diameter ~ 8 mm) with a vacuum ~ 10^{-5} Torr. The detailed procedure for obtaining glassy materials is discussed in our previous work [4]. Thin films of these glasses are prepared by vacuum evaporation technique keeping glass substrates at room temperature. The thickness of the films is ~ 500 nm. The co-planar structure of thin films (length ~ 1.2 cm and electrode separation ~ 0.12 mm) is used for the present measurements. The amorphous nature of thin films is confirmed by X-ray diffraction technique.

For the measurements of high field conduction, thin film samples are mounted in a specially designed sample holder. A vacuum ~10^{-2} Torr is maintained throughout the measurements. A d. c. voltage (0 to 300 V) is applied across the sample and the resultant current is measured by a digital Pico-Ammeter. I – V characteristics are measured at various fixed temperatures in these films. 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

It is observed that, at low electric fields (<10^3 V/cm), an ohmic behavior is observed. However, at high electric fields (~10^4 V/cm), a superohmic behavior is observed.

According to the theory of space charge limited conduction, in 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 [10]

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

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

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

As evident from eqs. (1) and (2), in 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 glassy $Ge_{20}Se_{80-x}Ag_x$ (x = 0, 10, 15, 20) and $(Ge_{20}Se_{80})_{100-x}Pb_x$ (x = 0, 2, 4, 6) systems, space charge limited conduction is reported in our previous work [8, 9]. By fitting the experimental data to the theory of space charge limited conduction, density of defect states near Fermi level is calculated for the above glassy systems. The density of localized states (g_0) is plotted against Ag concentration in Fig.1 and against Pb concentration in Fig. 2.

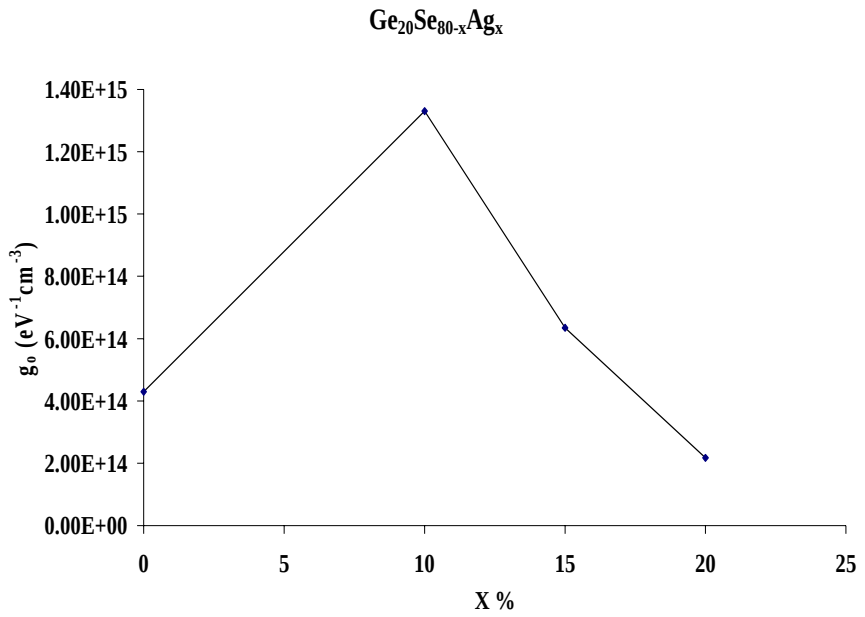

Fig. 1 The density of localized states (g_0) versus Ag concentration

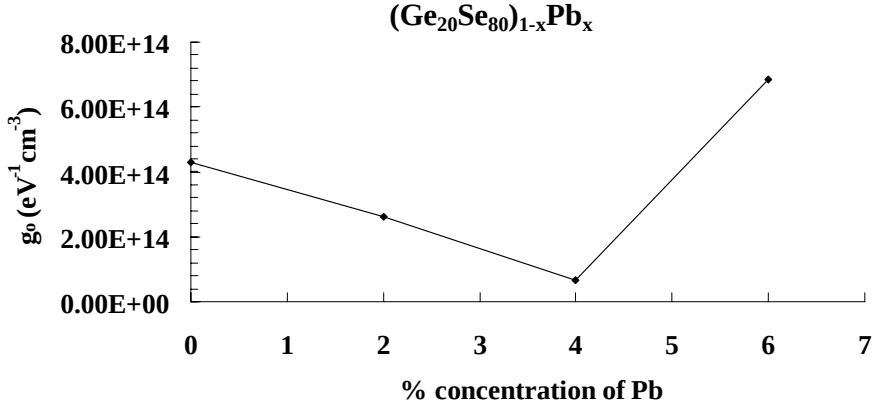

Fig. 2 The density of localized states (g_0) versus Pb concentration

In $Ge_{20}Se_{80-x}Ag_x$ system, the density of defect states increases with the increase of Ag concentration upto 10 at % of Ag due to smaller electronegativity of Ag [11] as compared to binary $Ge_{20}Se_{80}$ alloy. However, at higher concentration of Ag, the density of defect states decreases with Ag concentration. This can be explained in terms of change in structure of chalcogenide glasses from two-dimensional layered structure to a three-dimensional network arrangement due to cross-linking at a particular average co-ordination number <z> = 2.7 as reported by Tanaka [12]. In this glassy system, such a transition is observed at <z> = 2.6 which is close to the above value of <z>.

However, it is interesting to note that in case of $(Ge_{20}Se_{80})_{1-x}Pb_x$ system, the density of defect states decreases on incorporation of Pb upto 4 at%, though Pb has lesser electronegativity than binary $Ge_{20}Se_{80}$ alloy. The increase of the density of defect states at higher concentration of Pb is also observed in the above glassy system. This type of change in the composition dependence of density of defect states is observed at an average co-ordination number <z> = 2.4 which is reported in the literature [13] due to the formation of stable glass at this value of <z>.

The above results indicate that the behaviour of Pb is different in binary $Ge_{20}Se_{80}$ alloy as compared to other additives such as Ag. The different behavior of Pb additive in binary Ge-Se system is also well known in the literature [2] as p to n transition is observed at a particular concentration of Pb in this glassy system while no such transition has been reported with Ag.

It is now well established that the metallic additives such as Pb enters the network of Ge-Se system as charged species, altering the concentration of valence alteration pairs [14, 15]. When the concentration of charged additives exceeds that of valence alteration pairs, the chalcogenide glasses exhibit the p to n transition.

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) and $(Ge_{20}Se_{80})_{100-x}Pb_x$ (x = 0, 2, 4, 6) at different temperatures. At low fields ($<10^3$ V/cm), an ohmic behavior is observed. However, at high fields (~ 10^4 V/cm), a super ohmic behavior is observed. In $Ge_{20}Se_{80-x}Ag_x$ system, the density of defect states increases with the increase of Ag concentration upto 10 at % of Ag due to smaller electronegativity of Ag as compared to binary $Ge_{20}Se_{80}$ alloy. However, at higher concentration of Ag, the density of defect states decreases with Ag concentration. However, in case of $(Ge_{20}Se_{80})_{100-x}Pb_x$ (x = 0, 2, 4, 6) system, the density of defect states decreases on incorporation of Pb up to 4 at%, though Pb has lesser electronegativity than binary $Ge_{20}Se_{80}$ alloy. This shows that the behavior of Pb is different in binary $Ge_{20}Se_{80}$ alloy as compared to other additives such as Ag.

References

[1] P. Nagel, H. Ticha, L.Tichy, A. Triska, J. Non-Cryst. Solids **59**, 1015 (1983).
[2] N. Tohge, H. Matsuuo, T. Minami, J. Non-Cryst. Solids **95,** 809**(**1987).
[3] S. Kohli, V. K.Sachdeva, R. M. Mehra, P. C. Mathur, Phy. Stat. Sol. (B) **209**,389 (1998).
[4] M. A. Majeed Khan, M. Zulfequar, M. Husain, Physica B **366**, 1 (2005).
[5] S. M. El-Sayed, Vacuum **65,** 177 (2002).
[6] V. S. Kushwaha, A. Kumar, J. Mater. Sci. **42,** 2712 (2007).
[7] S. Kumar, R. Arora, A. Kumar, Solid State Commun. **82,** 725 (1992).
[8] V. S. Kushwaha, S. Kumar, A. Kumar, Euro. Physical J. App. Physics **35,** 149 (2006)
[9]V. S. Kushwaha, A Kumar, J. Non-Cryst. Solids **353,** 4718 (2007).
[10] M. A. Lampert, P. Mark, Current Injection in Solids. Academic Press, New York: 1970.
[11] http://www.capital.net/com/vcl/periodic/periodic.htm
[12] K. Tanaka, Phys. Rev. B **39,** 1270(1989).
[13] J. C. Phillips, M. Thorpe, Constraint theory and stiffness percolation in network glasses, P. M. Duxbury (eds.). Kluwer Academic Press, **155** (1999).
[14] N. Tohge, T. Minami, Y. Yamamoto, M. Tanaka, J. Appl. Phys. **51,** 1048 (1980).
[15] K. L. Bhatia, G. Parthasarathy, A. Sharma, E. S. R. Gopal, Phys. Rev. B **38,** 6342 (1988).