A.C. conduction in glassy alloys of $Se_{90}Sb_{10-x}Ag_x$

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ABSTRACT

Temperature and frequency dependence of a.c. conductivity is studied in glassy $Se_{90}Sb_{10-x}Ag_x$ ($x=2, 4, 6$ and 8) in the temperature range (288–358 K) and frequency range (1–500 kHz). An agreement between experimental and theoretical results suggests that the behavior of glassy Se–Sb–Ag system can be successfully explained by correlated barrier hopping (CBH) model. The results show that bipolaron hopping dominates over single polaron hopping in present case, which is explained in terms of lower value of potential barrier. By fitting the experimental data to CBH model, the density of charged defect states is calculated for all the glasses studied. The composition dependence of the density of these states is studied and found to show a maxima at 6 at% of Ag which is explained in terms of the mechanically stabilized structure at a particular average co-ordination number.

1. Introduction

The physical properties of chalcogenide glasses have attracted much interest due to their wide technical applications [1–5] in optoelectronic devices and also due to their use in optical components in infrared region. Besides, the physical properties of these semiconducting glasses are strongly dependent on their composition [6]. These semiconductors have truly emerged as multipurpose materials and have been used to fabricate technologically important devices such as solar energy conversion [7–9], rewritable optical recording [10,11] infrared detectors [12] optical mass memories [13], holography [14], holographic recording media and programmable metallization cell memories [15], ultrasonic delay lines [16], and optical fibers [17]. Such wide ranging applications are possible due to some unique phenomenon like photo-induced structural transformations [18], photo-darkening/bleaching [19] etc. Unlike that of crystals, conductivity of chalcogenide glasses is little affected by doping. This is due to defect states in the band gap which pin the Fermi level. Many electrical properties are also affected due to the presence of defects. The determination of defect density in these glasses has, therefore, always been an important problem in this area. To investigate the nature of defect states in amorphous systems the measurement of a.c. conductivity has been a widely used tool. It is assumed that these defect centers are responsible for a.c. conduction.

A.C. conductivity has been observed in chalcogenide glasses even at low frequency as low as 100 Hz. This is expected if one assumes the hopping of charge carrier (electron) between charged defect states suggested for chalcogenide glasses [20]. A.C. conductivity is found to vary with frequency and temperature [21–26]. Various models have been suggested to explain this behavior. From the experimental data, density of defect states has also been evaluated by various workers.

Silver doped chalcogenide glasses have drawn great interest of scientists due to their application in many fields which include phase change memories, programmable metallization cells, sensors, batteries etc [27,28]. As the silver doped chalcogenide glasses have low crystallization activation energy they provide high phase change rate thereby reducing the write time [28]. Further, the electrical resistivity after addition of silver is found to decrease by several orders of magnitude [27–29] which lowers the switching voltage and hence the energy required for storing the information reduces. Crystallization kinetics of silver doped glasses of Se–Sb system has already been reported by our group [30]. The present paper reports the a.c. conductivity measurements in $Se_{90}Sb_{10-x}Ag_x$ glasses as a function of frequency and temperatures. Density of defect states has also been evaluated from these measurements, which is found to vary with Ag concentration. Composition dependence of defect density is explained in terms of mechanically stabilized structure at a particular average co-ordination number.

2. Experimental

For the preparation of glassy alloys of $Se_{90}Sb_{10-x}Ag_x$ ($2 \leq x \leq 8$) exact proportions of high purity (99.999%) Se, Sb and Ag elements were weighed according to their respective atomic percentages

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with the help of an electronic balance (LIBROR, AEG-120) having least count of 10^{-4} g. Glassy alloys were prepared by a quenching technique. For this purpose the materials were sealed in evacuated quartz ampoules having dimensions of approximately 5 cm in length and 8 mm internal diameter. These ampoules along with materials were then heated upto a temperature of 800 °C at the rate of 3–4 °C per minute and kept at the same temperature for about 12 h. The ampoules were constantly rocked for the preparation of homogeneous alloys.

The alloys were ground to get very fine powder to prepare pellets by compressing the powdered alloy under a pressure of 5–6 tons in a die. Both faces of the pellets were coated with Indium so that good electrical contact could be achieved. For a.c. conductivity measurements, the pellets were mounted inside a sample holder where a vacuum $\sim 10^{-2}$ Torr is maintained during measurements. The temperature inside the sample holder is measured by a copper–constantan thermocouple mounted near the pellet. A digital LCR meter is used to measure a.c conductance at different frequencies.

3. Theoretical basis

To explain a.c. conductivity in semiconductors, it is assumed that a pair of localized states exists in which electrons move back and forth with a particular relaxation time. In amorphous semiconductors, pairs may have different relaxation times as the localized states may be considered to be randomly distributed in the space. The a.c. conductivity then will be sum of contributions from all such pairs. It has been reported in many glasses and amorphous materials that a.c. conductivity depends on frequency which follows the following equation [31,32]:

$$\sigma_{ac} \propto \omega^s, \quad \text{with } s \leq 1 \tag{1}$$

The a.c. conduction in amorphous glassy semiconductors is explained by the correlated barrier hopping (CBH) model developed by Elliot [33]. In this model it is assumed that a bipolaron hopping process occurs where two electrons simultaneously hop over a potential barrier between two defect states (D^+ and D^-). The height of the barrier depends on Coulombian interaction. Furthermore, it was suggested by Shimakawa [34] that at higher temperatures, D^0 states are thermally produced from D^+ and D^- states and single polaron hopping process becomes dominant.

In CBH model, the electrons in charged defect states hop over the Coulombic barrier of height W which is given as

$$W = W_m - \left(\frac{ne^2}{\pi \varepsilon \varepsilon_0 r}\right), \tag{2}$$

Where W_m is the maximum barrier height, ε is the dielectric constant, ε_0 is the permittivity of free space, r is the distance between hopping sites and n is the number of electron involved in a hop.

The relaxation time, τ, for the electron to hop over a barrier of height, W, is given by

$$\tau = \tau_0 \exp\left(\frac{W}{kT}\right), \tag{3}$$

where τ_0 is a characteristic relaxation time which is of the order of an atomic vibrational period and k is the Boltzmann constant. The a.c. conductivity, $\sigma_{ac}(\omega)$, for bipolaron hopping originating from intimate D^+ and D^- pairs having a non-random distribution can be written as

$$\sigma_{ac}(\omega) = \left(\frac{1}{6}\right) n \pi^3 \varepsilon \varepsilon_0 N N_P \omega (R_\omega)^6 \exp(e^2/4\pi \varepsilon \varepsilon_0 k T_g R_\omega) \tag{4}$$

where the hopping distance R_ω is given by

$$R_\omega = \left(\frac{ne^2}{\pi \varepsilon \varepsilon_0 W_m}\right)\left[1 + \frac{kT}{W_m \ln(\tau_0 \omega)}\right]^{-1} \tag{5}$$

Here N is the density of localized states at which carriers exists, N_P is the density of localized states to which the carriers hop, T_g, is the glass transition temperature and $n=2$ and $n=1$ for bipolaron and single polaron hopping, respectively. The maximum height W_m is regarded as the band gap.

According to CBH model, the frequency exponent 's' is given by

$$s = 1 - \frac{6kT}{W_m - kT\ln\left(\frac{1}{\omega \tau_0}\right)} \tag{6}$$

The frequency exponent 's' is both frequency and temperature dependent for small values of W_m/kT, 's' increases with increasing frequency and for large values of W_m/kT, 's' is nearly unity and the increase is so small that 's' is effectively independent of frequency. Eq. (6) also predicts that 's' decreases with increasing temperature and at low temperature, 's' decreases approximately linearly from the $T=0$ value of unity.

The a.c. conductivity $\sigma_{ac}(\omega)$ for single polaron hopping originating from randomly distributed defects centers can be expressed by the following equation as suggested by Shimakawa [34]:

$$\sigma_{ac}(\omega) = \pi^3 \varepsilon \varepsilon_0 N N_P \omega (R_\omega)^6 / 6 \tag{7}$$

where

$$R_\omega = \left(\frac{e^2}{\pi \varepsilon \varepsilon_0 W_m}\right)\left[1 + \frac{kT}{W_m \ln(\tau_0 \omega)}\right]^{-1} \tag{8}$$

The maximum barrier height, W_m, for single polaron hopping process is taken as half of the band gap.

Generally, a.c. conductivity of the chalcogenide glasses can be expressed as:

$$\sigma_{ac}(\omega) = [\sigma_{ac}(\omega)]_s + [\sigma_{ac}(\omega)]_b \tag{9}$$

Where $[\sigma_{ac}(\omega)]_s$ and $[\sigma_{ac}(\omega)]_b$ are the a.c. conductivities for single polaron hopping originating from randomly distributed defect states (Eq. (7)) and bipolaron hopping originating from non-random distribution of defect states Eq. (4) respectively.

4. Results and discussion

4.1. Frequency dependence of a.c. conductivity

The frequency dependence of a.c. conductivity for the glassy alloy of $Se_{90}Sb_8Ag_2$ at different temperatures is shown in Fig. 1. These curves show that $\ln(\sigma_{ac})$ vs $\ln(\omega)$ curves are almost straight lines indicating that they follow the relation given in Eq. (1). The decrease in slope indicates that the frequency exponent 's' decreases with increase in temperature. This is consistent with the CBH model as mentioned above.

4.2. Temperature dependence of a.c. conductivity

The temperature dependence of a.c. conductivity for a-$Se_{90}Sb_8Ag_2$ alloys at different frequencies ranging from 500 Hz to 500 kHz is shown in Fig. 2. These curves show that a.c. conductivity varies slowly at lower temperature and there is strong temperature dependence at higher temperatures.

As mentioned in Section 3, the a.c. conductivity in amorphous chalcogenide alloys may be considered as the sum of two types of conduction mechanisms, i.e., single polaron hopping and bipolaron hopping. Considering this, the experimental data has been