J Mater Sci (2007) 42:2712–2716
DOI 10.1007/s10853-006-1407-7

Study of defect states in a-$Se_{85}Te_{15-x}Pb_x$ thin films by space charge limited conduction mechanism

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Received: 16 November 2005 / Accepted: 17 February 2006 / Published online: 4 January 2007

Abstract Current–Voltage (*I–V*) characteristics have been studied at various temperatures in vacuum evaporated thin films of a-$Se_{85}Te_{15-x}Pb_x$ (x = 0, 2, 4, 6) alloys. These characteristics show that, at low electric fields, an ohmic behaviour is observed. However, at high electric fields ($E \sim 10^4$ V/cm), the current becomes superohmic. At high fields, in case of samples having 0 and 2 at% of Pb, the experimental data fits well with the theory of space charge limited conduction (SCLC) in case of uniform distribution of localized states in the mobility gap. Such type of behaviour is not observed at higher concentration of Pb in the present glassy system due to high conductivity. In these samples, joule heating due to large currents may prohibit the measurement of SCLC. Using the theory of SCLC for the uniform distribution of the traps, the density of localized defect states near Fermi level is calculated for these compositions. The results indicate that the density of defect states near Fermi level increases on addition of Pb to binary $Se_{85}Te_{15}$alloy. This is explained in terms of electronegativity of Pb as compared to host elements.

Introduction

Chalcogenide glasses are promising materials for many applications in solid-state devices. Recently, special interest have been drawn in the amorphous thin films of chalcogenide glasses in connection with the modification of their properties on doping with metal impurities [1]. In thermally evaporated amorphous films of chalcogenide glasses, these impurity atoms are electrically active and allow to obtain new materials with the improved properties. Se–Te alloys have drawn great attention due to their higher photosensitivity, greater hardness and higher crystallization temperature as compared to pure glassy Se. It is widely accepted that the addition of third element in binary chalcogenide glasses is found to be useful in obtaining stable glassy alloys due to cross-link structure. Electrical, optical, thermal and photoconductive properties have been studied by many workers [2–6] as Pb incorporation in chalcogenide glasses show transition from *p* type conduction to *n* type conduction at certain atomic percentage of Pb [7, 8]. The effect of this impurity on the density of defect states (DOS) has always been a subject of curiosity as the knowledge of this parameter is a key parameter in chalcogenide glasses for determining the semiconducting properties of theses materials.

To measure this quantity, different methods have been used with all their advantages and their limitations. One of the most direct methods for the determination of DOS involves the measurements of space charge limited conduction. In these materials, density of defect states reported by different groups [9–14] ranges from 10^{13} to 10^{17} eV^{-1} cm^{-3}

High field effects are observed in these materials and the results have been interpreted in terms of heating effect, space charge limited conduction [9–19] or in terms of high field conduction due to Poole-Frenkel or Schottky effect [20–26]. The present paper

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reports the space charge limited conduction measurements in thin films of a-$Se_{85}Te_{15-x}Pb_x$ (x = 0, 2, 4, 6).

Experimental

Glassy alloys of $Se_{85}Te_{15-x}Pb_x$ (x = 0, 2, 4, 6) were prepared by quenching technique as described elsewhere [5]. The glassy nature of the materials was checked by XRD technique. X ray diffraction pattern for $Se_{85}Te_{15}$ is given in Fig. 1. XRD pattern for other compositions were also of the same nature

Thin films of these glasses were prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at bottom were used for the electrical contact. The thickness of the films was measured by optical methods and was 500 ± 10 nm. Thickness was kept almost constant to avoid thickness effects on the electrical parameters. The co-planar structure (length ~1.2 cm and electrode separation ~0.12 mm) was used for the present measurements. The films were kept in deposition chamber in the dark for 24 h before mounting them in the sample holder. This was done to allow sufficient annealing at room temperature so that a metastable thermodynamic equilibrium may be attained in the samples. The deposition parameters were kept almost the same for all the samples so that a comparison of results could be made for the various glassy samples. The amorphous nature of thin films was ascertained by x-ray diffraction.

For the measurements of high field conduction, thin film samples were mounted in a specially designed sample holder. A vacuum ~10^{-2} Torr was maintained throughout the measurements. A d.c.voltage (0 to 300 V) was applied across the sample and the resultant current was measured by a digital Pico-Ammeter. *I–V* characteristics were measured at various fixed temperatures (295–343 K) in these films. The temperature of the films was controlled by mounting a heater inside the sample holder and measured by a calibrated copper-constantan thermocouple mounted very near to the films. Before measuring *I–V* characteristics, thin films were annealed in a vacuum ~10^{-2} Torr near glass transition temperature for 2 h in the same sample holder that was used for the above measurements.

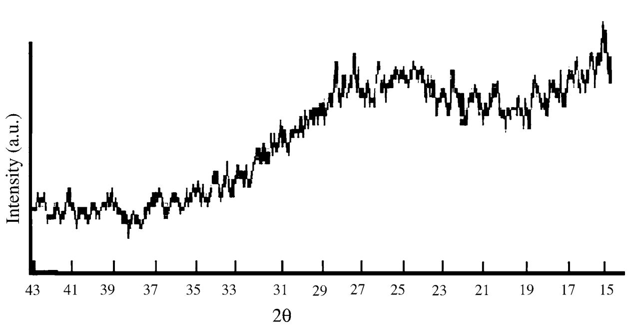

Fig. 1 X ray diffraction pattern for $Se_{85}Te_{15}$ alloy

The primary errors in the data and error in the slope have been estimated by least square method and percentage of error is shown in figures by error bars using software program ORIGIN 6.1.

Results and discussion

I–V characteristics studied at different temperatures in all the glassy samples show that, at low fields (<10^3 V/cm), an ohmic behaviour is observed. However, at higher fields (~10^4 V/cm), a superohmic behaviour is observed in all the samples.

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.

According to the theory of space charge limited conduction, in the 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 [27]

$$I = (eA\mu n_0 V/d)\exp(SV) \tag{1}$$

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

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

As evident from Eq. (1) and (2), in case of space charge limited conduction, the ln I/V versus V curves should be a straight line and slope (S) of these curves should be inversely proportional to the temperature.

In the present case, at higher fields, ln (I/V) versus V curves are found to be straight lines at all the measuring temperatures in all the samples. Such curves for amorphous thin films of $Se_{85}Te_{15-x}Pb_x$ (x = 0, 2, 4, 6) are plotted in Fig. 2. The slope (S) of these curves is inversely proportional to the temperature for $Se_{85}Te_{15}$ and $Se_{85}Te_{13}Pb_2$ samples (Fig. 3). However, at high concentration of Pb, slope (S) increases with increase

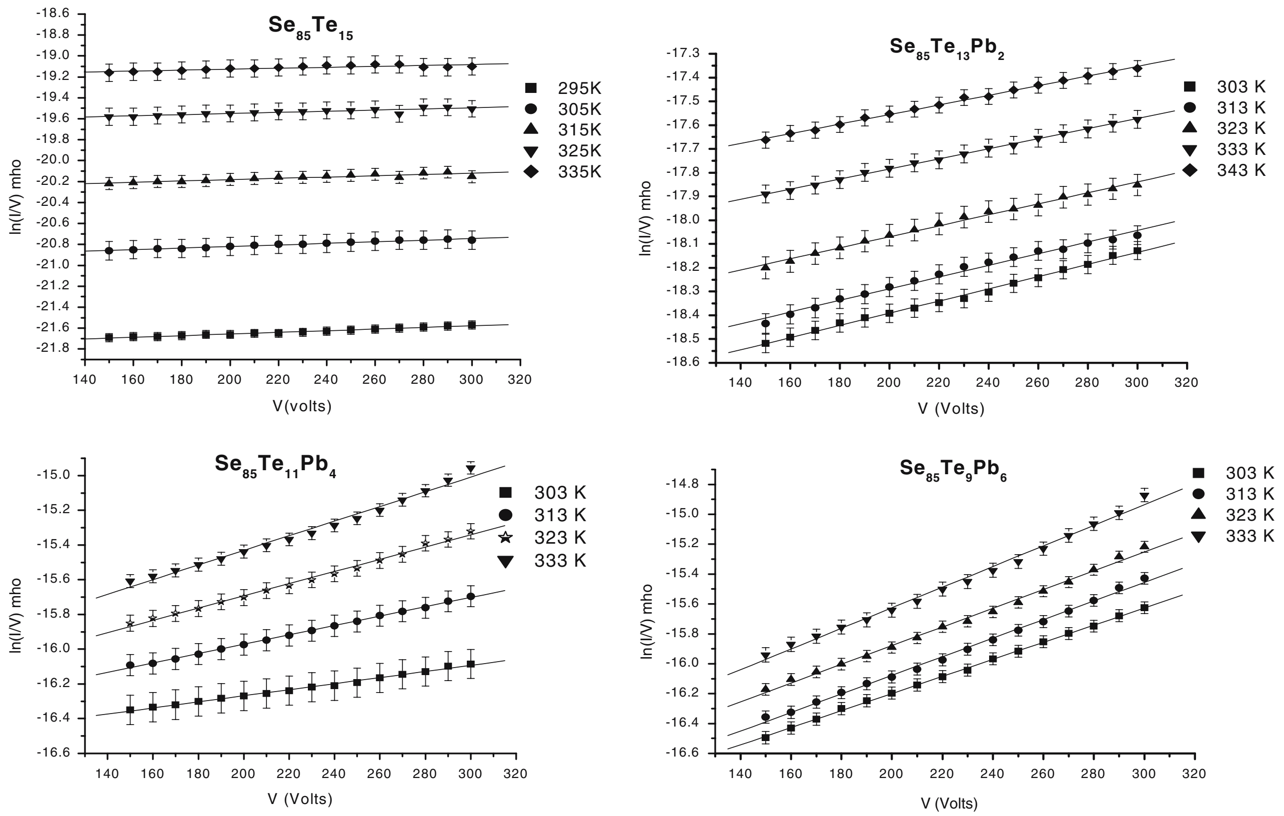

Fig. 2 ln I/V versus V curves at different temperatures for $Se_{85}Te_{15-x}Pb_x$ system

in temperature (Fig. 4), which is against the theory of SCLC. Due to higher conductivity, joule heating may be predominant which prohibits the measurement of SCLC in these samples. For further analysis of the results, we have therefore chosen the $Se_{85}Te_{15}$ and $Se_{85}Te_{13}Pb_2$ samples. In our earlier studies also, SCLC could be observed only at low concentration of Pb in a-$Se_{75}In_{25-x}Pb_x$ thin films [5].

Using Eq. 2, we have calculated the density of localized states from the slopes of Fig. 3. The value of the relative dielectric constant ε_r are measured by using capacitance measuring assembly model GR 1620 AP, employing the three terminal technique. The values of the relative dielectric constant and calculated values of density of defect states are given in Table 1. These

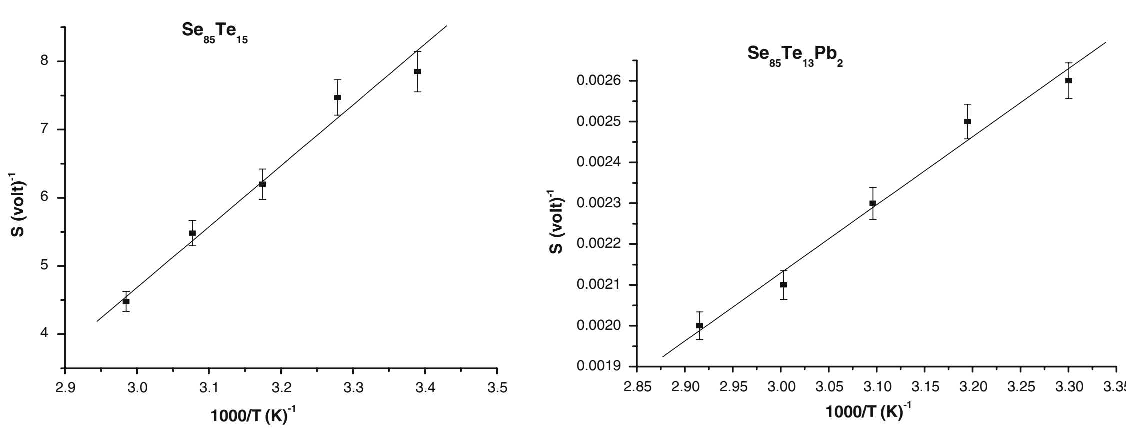

Fig. 3 Slope (S) versus $1000/T$ curves for $Se_{85}Te_{15}$ and $Se_{85}Te_{13}Pb_2$ thin films

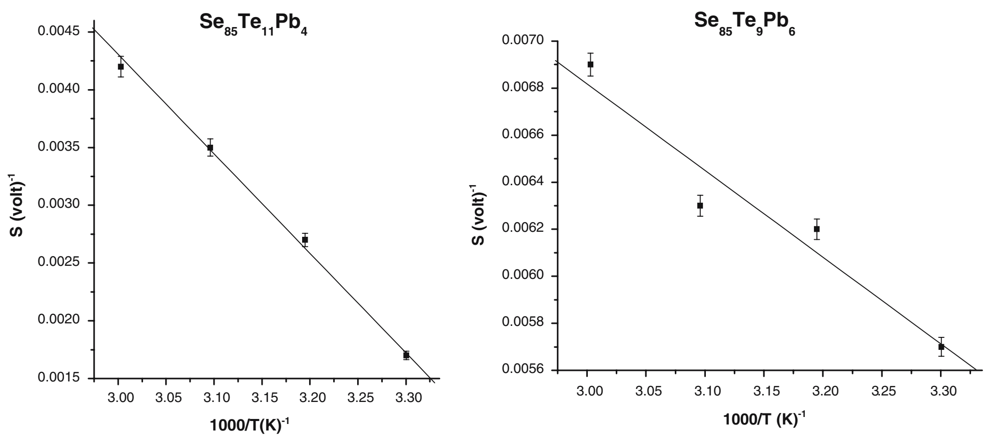

Fig. 4 Slope (S) versus 1000/T curves for $Se_{85}Te_{11}Pb_4$ and $Se_{85}Te_9Pb_6$ thin films

Table 1 Composition dependence of density of defect states (g_o) in a-$Se_{85}Te_{15-x}Pb_x$ (x = 0, 2) films

Samples	Slope of S versus 1000/T curve	ε_r (120 Hz, 303 K)	g_o (density of defect states in eV^{-1} cm^{-3})
a-$Se_{85}Te_{15}$	0.9×10^{-3}	7.78	7.68×10^{14}
a-$Se_{85}Te_{13}Pb_2$	1.7×10^{-3}	18.5	9.7×10^{14}

values agree with reported by other groups in chalcogenide materials.

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. [28] observed that, on introducing Cl to Se–Te system, the residual potential is decreased again. This result was interpreted on the basis of a structural defect model where Te was assumed to form positively charged impurities due to smaller electronegativity of Te as compared to Se [29], while Cl atoms having higher electronegativity than Selenium [29] form negatively charged impurities, thereby compensating the effect of Te [28]. Along the same lines, one can expect that when Te having lower electronegativity than Se [29] is introduced, positively charged defects will be created and on introducing the Pb having lower electronegativity than Se further increases the positively charged defects, thus increasing the density of defect states in $Se_{85}Te_{13}Pb_2$ as compared to pure Se [14] and $Se_{85}Te_{15}$.

In our earlier communication [2] we have reported that the photosensitivity decreases on the addition of Pb in binary $Se_{85}Te_{15}$ alloy. This indicates that the life time of the excess carriers is reduced on the addition of Pb. Lesser life time further indicates higher recombination rate for the excess carriers, which is expected when the density of defect states increases with the addition of Pb. The present results also indicate the increase in the density of defect states on introducing Pb to binary $Se_{85}Te_{15}$ alloy.

Conclusion

I–V characteristics have been studied in amorphous thin films of $Se_{85}Te_{15-x}Pb_x$ (x = 0, 2, 4, 6). At low fields (<10^3 V/cm), an ohmic behaviour is observed. However, at high fields (~10^4 V/cm), a super ohmic behaviour is observed.

Analysis of the observed data shows the existence of Space charge limited current in the samples having 0 and 2 at% of Pb. From the fitting of the data to the SCLC theory in case of uniform distribution of localized defect states in the mobility gap, the density of defect states near Fermi-level is calculated. The addition of Pb impurity in a-$Se_{85}Te_{15}$ increases the density of defect states. This is confirmed by the decrease of photosensitivity on the addition of Pb in a-$Se_{85}Te_{15}$. This is explained according to structural defect model based on the electronegativity difference.

At higher concentration of Pb, SCLC is not observed probably due to higher conductivity. Due to large currents at high voltages, joule heating may be predominant which prohibits the measurements of SCLC at higher concentration of Pb.

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