Journal of Ovonic Research Vol. 5, No. 4, August 2009, p. 87 - 94

THERMALLY STIMULATED CURRENTS IN a - $Se_{70}Te_{28}Zn_2$

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Thermally stimulated currents (TSC) have been measured at different heating rates in a - $Se_{70}Te_{28}Zn_2$ thin films. It has been observed that TSC peaks shift towards the higher temperatures at higher heating rates. Trap depth has been calculated using single trap analysis which is found to be approximately 0.2 eV.

(Received August 5, 2009; accepted August 17, 2009)

Keywords: Se-Te-Zn, Chalcogenides, Thermally stimulated currents; Trap depth

1. Introduction

Chalcogenide glasses are the special glasses, which belong to the group of non oxide glasses. These glasses are also mostly p type semiconductor due to the fact that the number of electron excited above the conduction band mobility edge is smaller than the number of holes below the valance band mobility edge [1]. They also contain positively and negatively charged defect states. The application of these glassy semiconductors included a very wide spectrum such computer memories, erasable high density optical memories [2], photoconductive applications such as photoreceptor in copying machines and X-ray imaging plates [3].

The presence of localized defect states may act as traps for the conduction of charge carriers in amorphous semiconductors. The parameters of traps are energy position, distribution character, capture cross section and trapping concentration. Traps parameters are different in different amorphous materials. These parameters are being used to determine the specific features of kinetics process in each case.

Se-Te alloys are thought to be promising media which can be used for phase change between an amorphous and crystalline state. These alloys are found to have some significant problems when used as a recording layer material in optical phase change technique (PC) [4, 5]. The two serious problems are the limited reversibility [6], low glass transition and crystallization temperature. These problems can be removed by adding third element as a chemical modifier in Se-Te binary alloys. A lot of work has been done on ternary chalcogenide glasses having different compositions like Se-Te-Sb, Se-Te-Ge, Se-Te-In [7-9]. In the present work, Zn has been added as a third element in binary Se-Te alloys to study the thermally stimulated currents.

The reason for the selection of Zn as a chemical modifier in Se-Te system is based on it's attractive and important applications in chalcogenide glasses. Like Ag, Zn can also be used for photo - doping in chalcogenide glasses [10-15]. There are successful reports of doping of Zn Se_x Te_{1-x} in the literature that are suitable for the development of light emitting diodes and lasers.

Thermally stimulated current technique is a useful method for studying the defect states in semiconductors and insulators. [16-21]. According to this method traps are filled by a photoexitation of semiconductor at low enough temperature such that upon ceasing the illumination, trapped carrier can not be freed by thermal energy available at that temperature. The temperature is then raised at a constant rate. The liberated carriers contribute in an applied field, to an excess current until they recombine with carriers of opposite type or join the equilibrium carrier distribution. This excess current measured as a function of temperature during heating is called a thermally stimulated current For a single trap level, a TSC curve has one maxima whose position depends on capture cross section, heating rate and the trap depth .If discrete distribution of traps are present, TSC curve may consist of several peaks, each originating from distinct trap energy. By varying heating rates the trap depth & capture cross-section can also be determined by this method [22-23]. The present work is an attempt to study thermally stimulated currents in a-$Se_{70}Te_{28}Zn_2$ thin films and to obtain initial information about the trap depth.

2. Theory of measurements

There are several methods in literature to study the thermally stimulated currents and to determine activation energy of traps from experimental TSC curve. We chose the simplest case in which only one trap level is contributing to the TSC at a time. Although chalcogenide glasses may have trap distributed throughout the mobility gap, it appears justifiable to use the single trap analysis to calculate the trapping parameters in the present case, in view of the analysis of Simmson et al. [24-25]. We summarize the results for a single trap level, in the slow and fast re-trapping limit, and show how the trap parameters can be calculated in this case.

Slow re-trapping means that the probability of recapture of thermally liberated carries by traps is much smaller than recombination, whereas in fast re-trapping the recombination probability is small as compared to the recapture [26]. Both the cases have been treated in literature and one finds that the TSC for a material with a single trap level in the fast as well as slow re-trapping case is given by a general equation,

$$I(T) = A \exp. [- E_t / kT - B/\beta \int_{T_o}^{T} \exp. (- E_t / kT)\, dT] \tag{1}$$

Where parameters A and B are dependent on trapping centers and given in Table 1 for slow and fast re-trapping, β is the heating rate, k is the Boltzman constant, E_t is the trap depth. At a time t after the heating has started, the temperature T will be $T_0 + \beta t$, where T_0 is the initial temperature.

Table 1: Values of A and B for slow and fast re-trapping

Parameter	Fast	Slow
A	$q\, n_{to} N_e \mu E C / N_t$	$q\, n_{to} \nu \tau \mu EC$
B	$N_c / \tau\ N_t$	ν

.

n_{to} is the number of electrons in traps at t = 0, N_t is the total number of traps, q.is the electronic charge,ν is the escape frequency, E is the electric field, C is the crossectional area of the sample, N_c is the effective density of states in the conduction band and τ be the life time of electrons, μ is the mobility of electrons in conduction band.

For maxima to occur it is necessary that

$$d I(T) / dT \big|_{T=Tm} = 0 \tag{2}$$

i.e., from. equation (1)

$$\exp [E_t / kT] = B / \beta (k T^2_m / E_t) \tag{3}$$

From the above equation it is clear that, on increasing the heating rateβ, TSC maxima shifts towards the higher temperature.

$$\ln [B / \beta (k T^2_m / E_t)] = E_t / kT \tag{4}$$

This equation indicates that the graph between ln (T^2_m / β) and 1 / T_m would be straight line whose slope is related to E_t.

For temperature close to T_m, the contribution from the integral in equation (1) is quite small and the TSC at maxima can be approximated as [26].

$$I(T_m) = A \exp[-E_t / kT - 1] \tag{5}$$

If $E_t / kT >> 1$, then a plot of ln I (T_m) versus 1 / T_m will also be a straight line for different heating rates whose slope yields E_t / kT.

3. Experimental Procedure

(i)Material synthesis

Glassy alloy of $Se_{70}Te_{28}Zn_2$ was prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te and Zn elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated (~10^{-5} Torr) quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm). The ampoule containing material was heated to 800 ^{0}C and was held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3 - 4 ^{0}C / minute. During heating, the ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. This was done to obtain homogeneous glassy alloy. After rocking for about 12 hours, the obtained melt was rapidly quenched in ice-cooled water. The quenched sample was then taken out by breaking the quartz ampoule. The glassy nature of the alloy was ascertained by X-ray diffraction. For this, X-ray diffraction (XRD) patterns of sample were taken at room temperature by using an X-ray diffractometer (Philips, PW 1140/09). The copper target was used as a source of X-rays with $\lambda = 1.54$ Å (Cu $K_{\alpha 1}$).

(ii) Thin film preparation

Thin films of this glassy material of $Se_{70}Te_{28}Zn_2$ was prepared by

Vacuum evaporation technique keeping glass substrate at room temperature. Vacuum evaporated indium electrodes at bottom are used for electrical contacts .The thickness of the films is ~ 500 nm .The coplanar structures are used for the present measurements.

For TSC measurements, thin films were mounted in a specially designed sample holder which has transparent window to shine light .A vacuum of 10^{-2} torr is maintained throughout the measurements. The temperature of film is controlled by mounting heater inside the sample holder and measured by a calibrated copper – constantan thermocouple mounted very near to the film and the current is measured by Keithley electrometer model - 614. Before measurements the films were annealed first at 400K for one hour in a vacuum of 10^{-2} torr.

TSC measurements were performed at three different heating rates (0.069K/s, 0.104K/s, and 0.208 K/s) in a - $Se_{70}Te_{28}Zn_2$ films.

4. Results and discussion

In the present work, measurements have been done in two states at each heating rates, these two states are (1) temperature dependence of current before exposure of light (state I) and (2) same experiment after exposure of light (state II)

In the state I, sample is heated from room temperature 298K to 403K without any light exposure. In the II state, light is made incident on the sample for two minutes through the transparent window at room temperature. After switching off light, the decay of the photoconductivity was allowed for 10 min. Now, the sample is again heated up to 403 K at the same heating rate. These measurements were done at different heating rates.

From the above measurements we have observed that current in state (II)is higher than in state (I) which is clear from the Figs. 1 - 3. The difference of current in these two states is called thermally stimulated current (TSC).

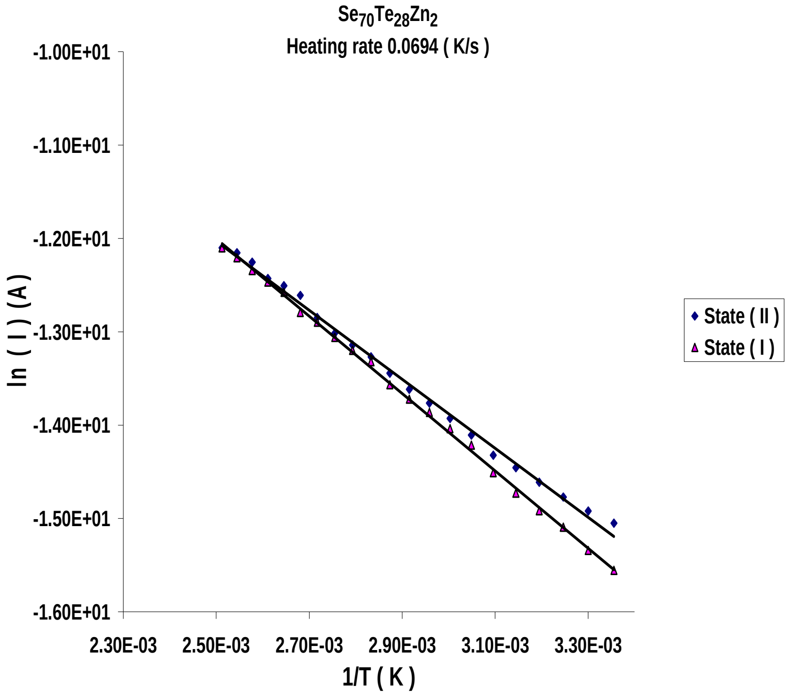

Fig1. Temperature dependence of current in state (I) and state (II) at a heating rate of 0.069 K / s.

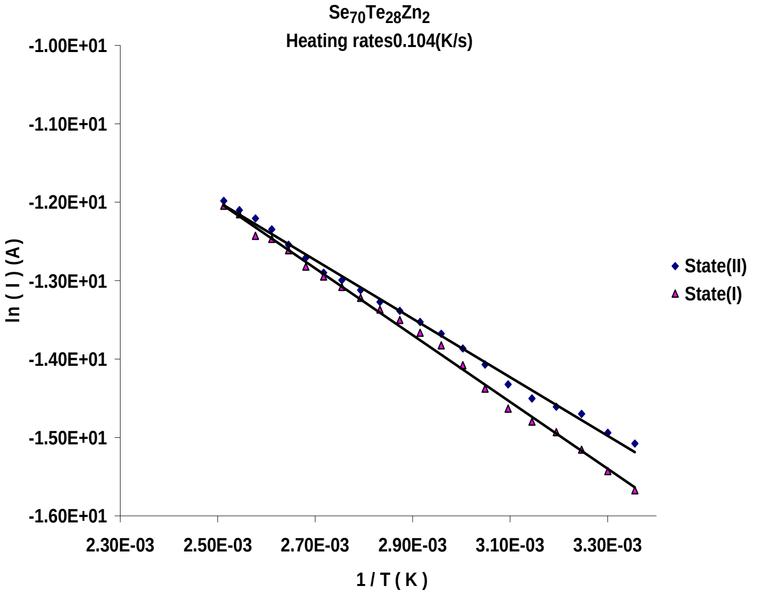

Fig2. Temperature dependence of current in state (I) and state (II) at a heating rate of 0.104 K / s.

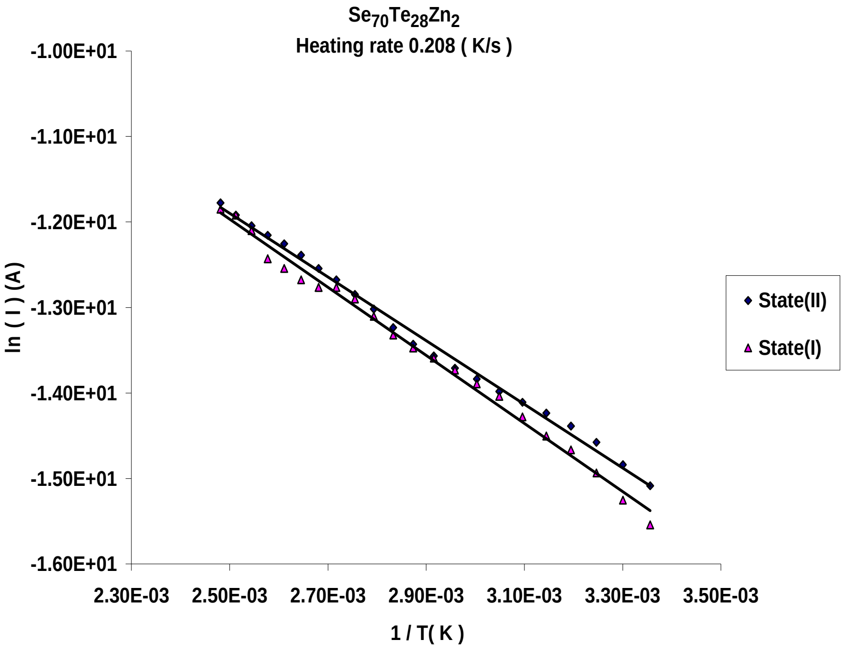

Fig. 3. Temperature dependence of current in state (I) and state (II) at a heating rate of 0.208 K / s.

TSC versus T curves show that the maxima in TSC is observed at a particular temperature T_m , which shifts towards the higher temperatures on increasing the heating rates β . Such a plot is shown in Fig.4.

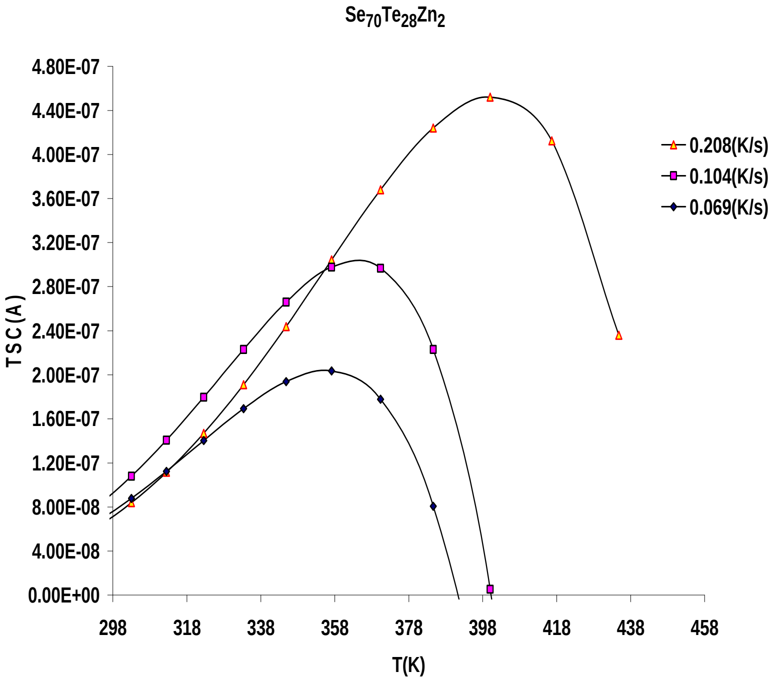

Fig4. Temperature dependence TSC in a-$Se_{70}Te_{28}Zn_2$ thin film at three different heating rates.

The theoretical equation 4 shows that ln (T^2_m / β) versus 1 / T_m curve should be straight line. In the present case also, such a plot (Fig. 5) shows a straight line between ln (T^2_m / β) and 1 / T_m whose slope gives the value of E_t which comes out to be 0.22 eV.

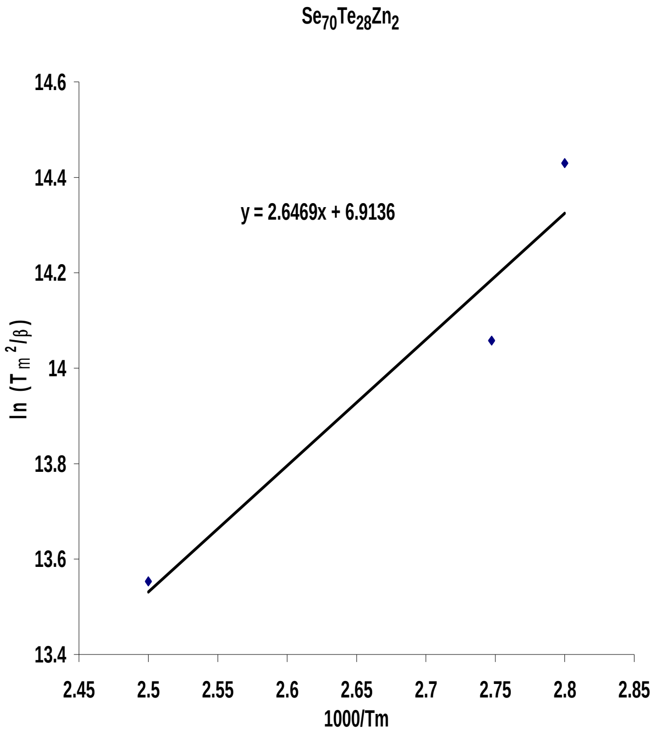

Fig.5. ln (T_m2 / β) against1000 / T_m curve in a-$Se_{70}Te_{28}Zn_2$ thin film.

Equation 5 indicates that a plot of the logarithmic of the current I (T_m) vesus1/ T_m should also be straight line. The values of T_m and their corresponding value of I (T_m) at different heating rates are mentioned in Table 2.

Table 2

Heating rate β (K / s)	Peak temperature T_m (K)	Current at peak temperature I (T_m) (A)
0.069	357	2.03E-07
0.104	364	3.04E-07
0.208	400	4.52E-07

From the above values a plot of the logarithmic of the current I (T_m) versus 1/ T_m curve is plotted and found straight line (Fig. 6). The slope of this curve is used to calculate the trap depth E_t which comes out to be 0.20 eV. The values of E_t calculated from both the plots ln (T^2_m / β) versus 1 / T_m and ln I (T_m) versus 1 / T_m are very close to each other, i.e., about 0.2 eV.

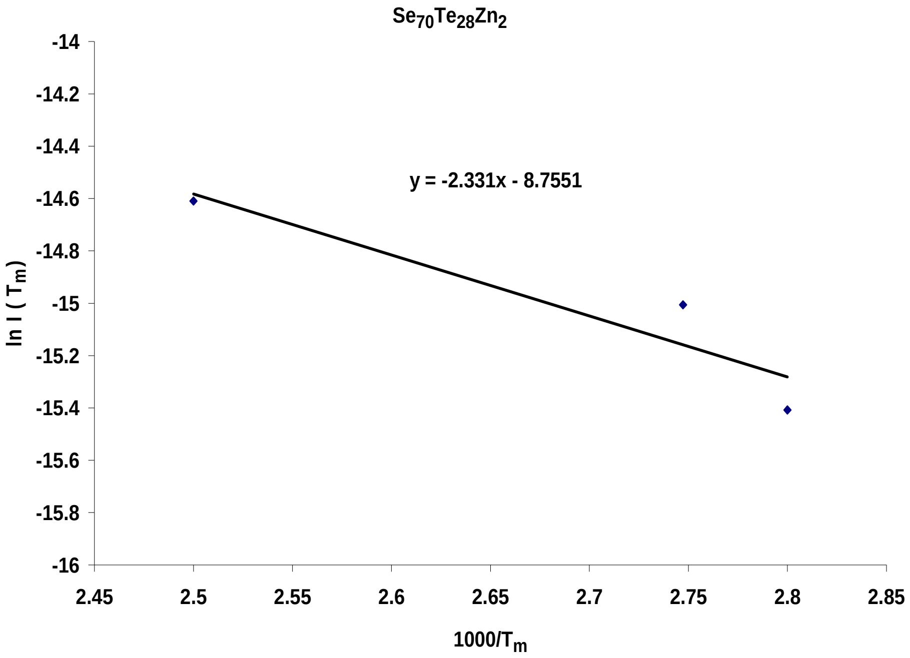

Fig. 6. ln I(T_m) against1000 / T_m curve in a-$Se_{70}Te_{28}Zn_2$ thin film.

The TSC measurements have been studied by various workers in binary alloys as well as in ternary alloys using different techniques. Recently, Kumar & Kumar [27] have reported thermally stimulated currents in thin films of a – $Se_{80-x}Te_{20}Ge_x$ and analyzed their data by the single trap level theory as used in present paper. They obtained trap depth 0.27 eV in their sample. Kushwaha et. al. [28] have also reported TSC measurements in thin film of a-$(Ge_{20}Se_{80})_{94}Pb_6$ alloys.

5. Conclusion

Thermally stimulated currents are measured at a three different heating rates. By using TSC data, trap depth is calculated which comes out to be 0.2 eV. Single trap analysis method is used for the calculation of trap depth.

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