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THERMALLY STIMULATED CURRENTS IN AMORPHOUS $Se_{60}Te_{20}Ge_{20}$

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The present paper reports the thermally stimulated current measurements in vacuum evaporated thin films of a- $Se_{60}Te_{20}Ge_{20}$. This composition is selected based on the highest photosensitivity at this composition in a- $Se_{80-x}Te_{20}Ge_x$ series. Well defined TSC peaks are observed in this case. The peaks shift to higher temperatures as heating rate is increased. Trap depth has been calculated from the heating rate dependence of peak temperature and also from the heating rate dependence of current at the peak temperature.

1. Introduction

In disordered materials and, primarily, in amorphous and glassy semiconductors, the individual groups of localized centers are energetically spread as it follows from theoretical studies. The presence of these localized states may act as traps for the charge carriers and hence affect many properties of these materials. Presumably, the parameters of traps (their energy position, the character of energy distribution, trapping concentration and cross-section for the charge carriers) are substantially different in various materials, and these parameters determine the specific features of kinetic processes in each case.

An important technique for studying the localized states in semiconductors is the method of thermally stimulated currents (TSC). In this method, traps are filled by the photoexcitation of the semiconductor, at a low enough temperature, such that upon ceasing the illumination the trapped carriers cannot be freed by the thermal energy available at that temperature. The temperature is then raised at a constant rate. The released carriers contribute, in an applied field, to an excess current until they recombine with carriers of the opposite type or join the equilibrium carrier distribution. This excess current, measured as a function of temperature during heating, is called a TSC curve.

A TSC curve for a single trap depth has one maximum whose position depends on the trap depth, the capture cross section of the trap, and the heating rate. By varying the heating rate, the trap depth and the capture cross section can be determined [1,2]. If a discrete distribution of traps is present, the TSC curve may consist of several peaks, each originating from a distinct trap energy.

For many years, it was believed that the physical properties of chalcogenide glasses can not be modified by foreign atoms. Doping could not be achieved by putting conventional impurities. However, recently, p to n transition has been reported [3-9] in binary Ge - Se, Ge - Se - Te and In - Se chalcogenide alloys, when third element is introduced in these glasses. Though the electrical and optical properties of these glasses have been studied by various workers [3-11], the measurements of thermally stimulated currents have not been reported.

In our previous communication [12], we have reported the photoconductive properties of glassy $Se_{80-x}Te_{20}Ge_x$ and found that the photosensitivity was the highest at x = 20. The present paper, therefore, reports the measurements of thermally stimulated currents in amorphous thin films of a-$Se_{60}Te_{20}Ge_{20}$ prepared by vacuum evaporation technique. These measurements were made at three heating rates (0.021 K/s, 0.027 K/s and 0.045 K/s).

Section 2 describes the theory of TSC used in the present study. The experimental details are given in section 3. The results have been presented and discussed in section 4. The conclusions have been presented in the last section.

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2. Theory of measurements

The simplest case is for the materials in which only one trap level is contributing to the TSC at a time. Although chalcogenide glasses may have traps distributed throughout the mobility gap, it appears justifiable to use the single trap analysis to calculate the trapping parameters of the present samples, in view of the analysis of Simmons et al. [13-14]. We summarize the results for a single trap level, in the slow and fast re-trapping limits, and show how the trap parameters can be obtained in this simple case.

Slow re-trapping means that the probability of recapture of thermally liberated carriers by traps is much smaller than recombination, whereas in fast re-trapping the recombination probability is small as compared to the recapture [15]. Both cases have been treated in the literature, and one finds that the TSC for a material with a single trap level in the fast as well as the slow re-trapping case is given by a general equation,

$$I(T) = A\exp\left[-\frac{E_t}{kT} - \frac{B}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E_t}{kT}\right)dT\right] \tag{1}$$

where A and B are dependent on the trapping centers and given in Table 1. E_t is the trap depth, β is the heating rate, T_0 is the initial temperature, and k is the Boltzmann constant. At a time t after the heating has started, the temperature $T = T_0 + \beta t$.

Table 1. Values of A and B for slow and fast retrapping cases.

Parameter	Fast	Slow
A	$Qn_{t0}N_e\mu EC/\ N_t$	$qn_{t0}\nu\tau\mu EC$
B	$N_c/\tau N_t$	ν

Table 1. Heating rate dependence of thermally (calculated Trap Depth (E_t) from Graph: 0.27 eV) stimulated current in a-$Se_{60}Te_{20}Ge_{20}$.

Heating Rate β (K/Sec)	T_m (K)	$1000/T_m$ (K^{-1})	$\ln(T_m^2/\beta)$ (K^{-1}sec)
0.021	313	3.1949	15.36
0.027	318	3.1447	15.14
0.045	333	3.0030	14.72

q. is the electronic charge, n_{t0} is the number of electrons in traps at t = 0, N_t is the total number of traps, μ is the mobility of electrons in the conduction band, ν is the escape frequency, τ is the lifetime of the electrons, E is the electric field, C is the cross-sectional area of the sample, and N_c is the effective density of states in the conduction band.

From equation (1) the condition of maxima in TSC (i.e., a peak in TSC) can be obtained by using the condition

$$\left.\frac{dI(T)}{dT}\right|_{T=T_m} = 0 \tag{2}$$

and is

$$\exp\left[\frac{E_t}{kT_m}\right] = \frac{B}{\beta}\frac{kT_m^2}{E_t} \tag{3}$$

Equation (3) predicts that the TSC maxima temperature (T_m) will shift towards higher temperature for a increase in β. Moreover, a plot of ln (T_m^2/β) versus $1/T_m$ should be a straight line whose slope is related to E_t.

Also, for temperatures close to T_m, the contribution from the integral in equation (1) is quite small and the TSC at maxima can be approximated as [15]

$$I(T_m) = A\exp\left[-\frac{E_t}{kT} - 1\right] \tag{4}$$

From equation (4), if E_t / kT_m >>1, a plot of ln $I(T_m)$ versus $1/T_m$ is a straight line for different heating rates, with slope $E_{t.}$

3. Experimental

Glassy alloy of a-$Se_{60}Te_{20}Ge_{20}$ is prepared by quenching technique. High purity (99.999 %) materials are weighed according to their atomic percentages and are sealed in quartz ampoules (length ~ 5 cm and internal dia ~ 8 mm) with a vacuum ~ 10^{-5} Torr. The ampoule containing the constituent 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 alloys.

After rocking for about 10 hours, the obtained melt is cooled rapidly by removing the ampoule from the furnace and dropping in ice-cooled water. The quenched sample of $Se_{60}Te_{20}Ge_{20}$ is taken out by breaking the quartz ampoule.

Thin films of this glass are prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at bottom are used for the electrical contact. The thickness of the films is ~ 500 nm. The co-planar structure (length ~ 1.4 cm and electrode separation ~ 0.5 mm) are used for the present measurements. Before measuring the conductivity, the films are first annealed at 340 K for one hour in a vacuum ~ 10^{-2} Torr.

Thin films samples are mounted in a specially designed sample holder, which has a transparent window to shine light. A vacuum ~10^{-2} Torr is maintained throughout the measurements. 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.

For TSC measurements thin film samples are mounted in a specially designed sample holder, which has a transparent window to shine light. A vacuum ~10^{-2} Torr is maintained throughout the measurements.

Sample is found to be ohmic up to 100 V. A voltage of 50 V is applied across the films and the resulting current is measured by a digital Pico-Ammeter. The temperature of the films is controlled by mounting a heater inside the sample holder, and is measured by a calibrated copper-constantan thermocouple mounted very near to the films. The heating rate is varied by applying different voltages across the heater.

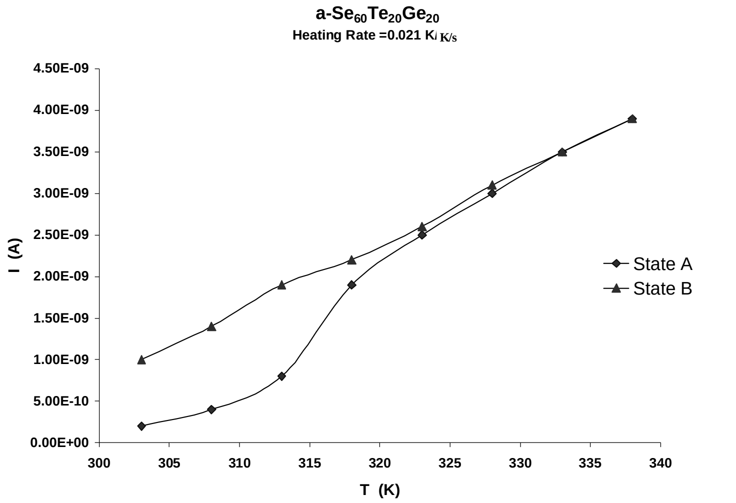

Fig. 1. Temperature dependence of dark current in a-$Se_{60}Te_{20}Ge_{20}$ before (State A) and after exposure to light (State B) at a heating rate of 0.021 K/s.

4. Results and discussions

TSC measurements were made in amorphous a-$Se_{60}Te_{20}Ge_{20}$ at three heating rates (0.021 K/Sec, 0.027 K/s and 0.045 K/s). At each heating rate the sample was first heated from room temperature (303 K) to 343 K without shining light (State A). Thereafter the sample is cooled down to room temperature again and light from a 200 W tungsten lamp, is shone on the sample through a transparent window for 2 minutes. Proper care was taken for the increase of temperature during light shining. After switching off the light, the photoconductivity was allowed to decay for 10 minutes. Then the sample was heated again to 343 K at the same heating rate (State B). These results are plotted in Fig. 1 - 3 for $Se_{60}Te_{20}Ge_{20}$ at three different heating rates. It is clear from these figures that the current in state B is higher then in state A. The difference of currents in these two states is called thermally stimulated current. The temperature dependence of TSC is plotted in Fig. 4 at all the three heating rates. It is clear from Fig. 4 that a maxima in TSC is observed at a particular temperature T_m. The position of TSC maxima shifts to higher temperatures as the heating rate is increased (see Fig. 4). The values of T_m at different heating rates are given in Table 1.

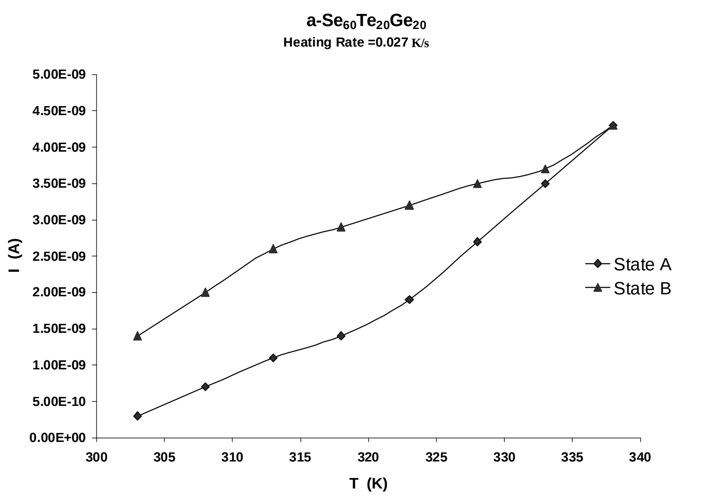

Fig. 2. Temperature dependence of dark current in a-$Se_{60}Te_{20}Ge_{20}$ before (State A) and after exposure to light (State B) at a heating rate of 0.027 K/s.

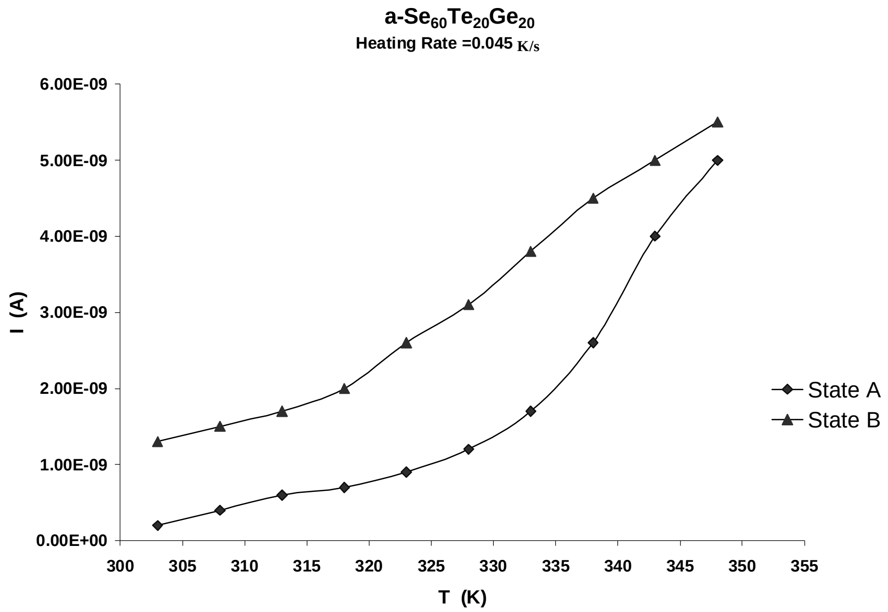

Fig. 3. Temperature dependence of dark current in a-$Se_{60}Te_{20}Ge_{20}$ before (State A) and after exposure to light (State B) at a heating rate of 0.045 K/s.

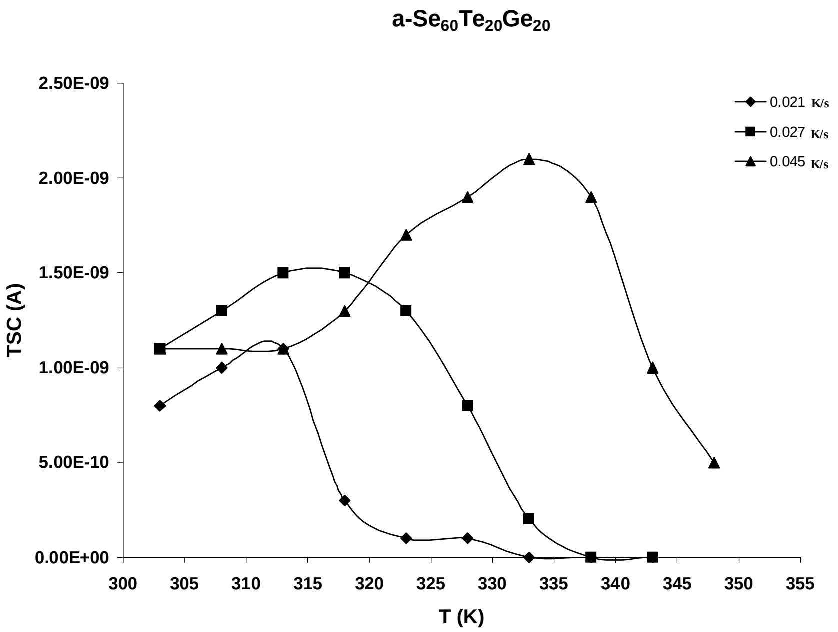

Fig. 4. Temperature dependence of thermally stimulated currents in a-$Se_{60}Te_{20}Ge_{20}$ at different heating rates.

As evident from equation 3, in case of TSC, $(T_m)^2$ / β vs 1 / T_m should be a straight line, whose slope will give the value E_t / k. Our experimental results also show a straight line curve in the plot $\ln(T_m)^2$ / β vs 1 / T_m (see Fig. 5). From the slope of this curve the trap depth E_t is calculated and found to be 0.27 eV. The shoulder at ~327 K at two heating rates can not be considered as TSC peak as this type of shoulder is not observed at all the heating rates. The experimental errors are within 2%.

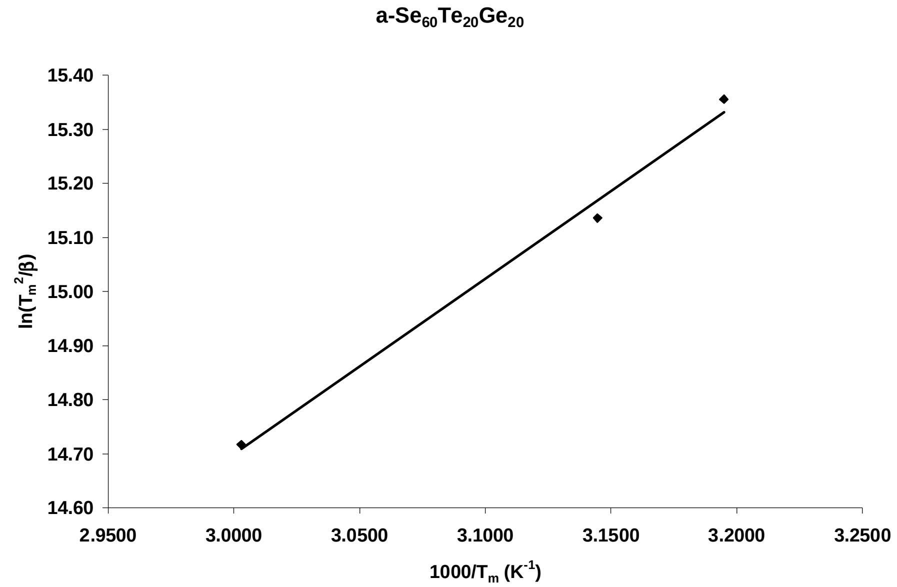

Fig. 5. $\ln(T_m{}^2/\beta)$ vs $1000/T_m$ in a-$Se_{60}Te_{20}Ge_{20}$ for three different heating rates.

Equation 4 shows that in case of TSC, current at the TSC maxima temperature, $\ln I(T_m)$ vs $1/T_m$ curve should be straight line whose slope will be E_t/k. The values of $I(T_m)$ and T_m at different heating rates are given in Table 2. These values are plotted in Fig. 6 and found that $\ln I(T_m)$ vs $1 / T_m$ curve is a straight line. From the slope of this curve E_t comes out to be 0.26 eV, which is very close to the value obtained from $(T_m)^2 / \beta$ vs $1 / T_m$ curve.

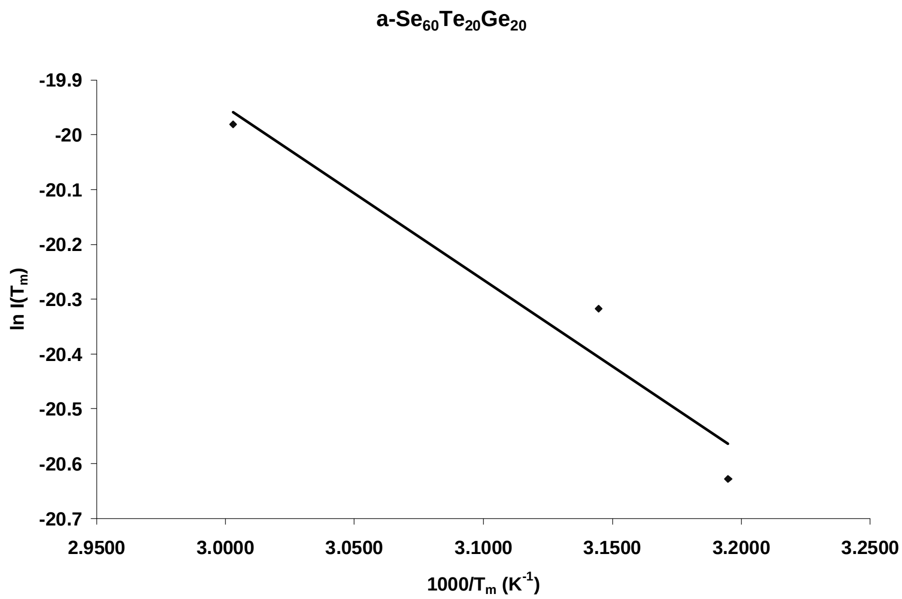

Fig. 6. $\ln I(T_m)$ vs $1000/T_m$ in a-$Se_{60}Te_{20}Ge_{20}$ for three different heating rates.

Table 2. T_m and $I(T_m)$ at Different Heating Rates in a-$Se_{60}Te_{20}Ge_{20}$.
(calculated trap depth (E_t) from Graph: 0.26 eV)

Heating Rate β (K/s)	T_m (K)	$1000/T_m$ (K^{-1})	$I(T_m)$ (A)	ln $I(T_m)$
0.021	313	3.1949	1.1×10^{-09}	-20.63
0.027	318	3.1447	1.5×10^{-09}	-20.32
0.045	333	3.0030	2.1×10^{-09}	-19.98

Hernandez et al. [16] have also reported thermally stimulated currents in glassy $CuIn_5Se_8$ sample and analyzed their data by the single trap level theory as used in the present paper. They found deep levels at 0.55 eV and 0.79 eV in their sample.

5. Conclusion

Thermally stimulated current measurements have been made in glassy sample of $Se_{60}Te_{20}Ge_{20}$. Well defined TSC peaks were observed. The peaks shift to higher temperatures as heating rate is increased. From the heating rate dependence of peak temperature and also from the heating rate dependence of current at the peak temperature, the trap depth is calculated which comes out to be 0.27 eV in this case.

References

[1] D. S. Misra, A. Kumar, S. C. Agarwal, Phil. Mag. B **49**, L 69 (1984).
[2] D. S. Misra, A. Kumar, S. C. Agarwal, Phys. Rev. B **31**, 1047 (1985).
[3] S. Kohli, V. K. Sachdeva, R. M. Mehra, P. C. Mathur, Phys. Stat. Sol. (b), **209**, 389 (1998).
[4] Z. H. Khan, M. Zulfequar, A. Kumar, M. Hussain, Can. J. Phys. **80**, 19 (2002).
[5] G. Mathew, J. Philip, J. Phys: Condensed Matter **11**, 5283 (1999).
[6] A. F. Maged, A. M. Sanad, M. F. El-Fouly, G. A. M. Amin, J. Mater. Res. **13**, 1128 (1998).
[7] M. Fadal, Ind. J. Pure, Appl. Phys. **37**, 57 (1999).
[8] A. M. Ahmed, N. M. Megahid, M. M. Ibrahiem, Ind. J. Pure & Appl. Phys. **41**, 863 (2003).
[9] O. El-Shazly, M. M. Hafiz, J. Mater. Sci: Materials in Electronics **12**, 395 (2001).
[10] D. K. Goel, C. P. Singh, R. K. Shukla, A. Kumar, Journal of Materials Science **35**, 1017 (2000).
[11] S. A. Khan, M. Zulfequar, M. Hussain, Physica B: Condensed Matter **324**, 336 (2002).
[12] D. Kumar, S. Kumar, Ind. J Pure & App. Phys (in press).
[13] J. G. Simmons, G. W. Taylor, Phys. Rev. B **4**, 502 (1971).
[14] J. G. Simmons, G. W. Taylor, M. C. Tam, Phys. Rev. B **7**, 3715 (1973).
[15] G. A. Dussel, R. H. Bube, Phys. Rev. **155**, 764 (1967).
[16] E. Hernandez, L. Duranl, C. A. Durante Richon, G. Aranguren, C. Guerrero, J. Naranjo, Cryst. Res. Technol **37**, 1227 (2002).