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Photoconductivity in Thin Film of a-$(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$

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Steady state and transient photoconductivity measurements have been done on thin film of a-$(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ as a function of temperature and intensity. Dark conductivity (σ_d) and photoconductivity (σ_{ph}) measurements show that the conduction in this glass is through an activated process having single activation energy in the temperature range 283–350 K. The intensity dependence of steady state photoconductivity (σ_{ph}) follows a power law with intensity (F), $\sigma_{ph} \propto F^{\gamma}$, where the power γ has been found between 0.5 and 1.0, suggesting bimolecular recombination. Rise and decay of photocurrent at different temperatures and intensities show that photocurrent (I_{ph}) rises monotonically to the steady state value and the decay of photocurrent is quite slow. A detailed analysis of photoconductive decay shows that the recombination within localized states may be predominant recombination mechanism in this glassy alloy. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Chalcogenide glasses have recently drawn great attention due to their potential use in various solid state devices [1, 2]. The common feature of these materials is the presence of localized states in the mobility gap [3] due to the absence of long range order as well as various inherent defects. In these materials, photocurrent behaviour is controlled by carrier localization and delocalization processes [4]. The steady state and transient photoconductivity may be used to determine the energy distribution of various species of gap states, which influence carrier mobilities and life time in these materials. The photoconductivity kinetics determined the process of trapping of non equilibrium charge carriers on localized centers of various depths [5], such studies are, therefore, important to understand the energy distribution of the traps. The temperature and intensity dependence of photoconductivity allow the identification of areas with monomolecular or bimolecular recombination behaviour.

Transient photoconductivity in chalcogenide glasses has received increasing attention in recent years. It is observed that under certain experimental conditions, the photoconductivity shows different behaviours. (i) The photocurrent passes through a maximum before the stationary sate is reached. (ii) The photocurrent rises upto the maximum and then settles down to the steady state as power function of time with exponents. Work on steady state and transient photoconductivity in chalcogenide glasses has been reported by many authors [6–9]. These measurements have been interpreted as revealing a broad featureless exponential tail of states above the valence band mobility edge [9], or in contrast, a fairly well defined set of recombination centres in the gap.

Chalcogenide glasses like Ge-Se are known to be very good covalently bonded glass formers. The structure of these glasses is a function of composition [3,10]. A discontinuity in various physical properties of these glasses has been observed at a composition when the average coordination number $<r> = 2.4$ [11]. The coordination number of Ge is 4 and Se is 2, so at x = 20, the value of $<r> = 2.4$ in a-Ge_xSe_{100-x} system. What happens to the $Ge_{20}Se_{80}$ system, when it is alloyed with a second element of group IV, is very important form the basic as well as application point of view. Sn belongs to the IV group and its atomic radii (1.41 Å) is more than the Ge (1.22 Å). Bond-stretching forces acting as constraints are present in Ge, Se and Sn. These bond bending constraints are important in Ge and Se but may be ignored in Sn because the corresponding spring constant is weak compared to Ge and Se. This fact makes Ge-Se-Sn, a useful system to study as the addition of Sn is expected to reduce the number of constraints per atom [12]. A lot of studies have

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been done on Ge-Sn-Se system at higher concentration of Ge (≥33) [12–14], but not much work has been done at lower concentrations of Ge (≥30).

The present paper reports the dark conductivity measurements on the thin film of a-$(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ as a function of temperature (283–350 K). This paper also reports the steady state and transient photoconductivity measurements on the thin film of a-$(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ as a function of temperature (283–350 K) and intensity (3-1035 Lux). Section 2 describes the experimental details of the sample preparation and photoconductivity measurements. The results are presented and discussed in Section 3. Last section deals with the conclusions of the present work.

2. Experimental procedure

A glassy alloy of $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ is prepared by quenching technique. Materials (5N pure) are weighed according to their atomic percentages and sealed in a quartz ampoule in a vacuum $\approx 2\times10^{-5}$ mbar. The sealed ampoule is kept inside a furnace where the temperature is increased upto 1250 K at a heating rate of 2–3 K/min. The ampoule is frequently rocked for 24 h at the highest temperature to make the melt homogeneous. The quenching is done in liquid N_2. Thin films of the glassy alloy have been prepared by vacuum evaporation technique keeping substrates at room temperature and base pressure $\approx 2\times10^{-5}$ mbar, using a Molybednum boat. Pre-deposited thick Indium electrodes on well-degassed Corning 7059 glass substrates have been used for the electrical contacts. A planar geometry of the film (length ≈ 1.78 cm; electrode gap $\approx 8\times10^{-2}$ cm) is used for the electrical measurements. The thickness of the film is ≈ 5000 Å. The film has been kept in the deposition chamber in dark for 24 hours before mounting in the metallic sample holder to attain thermodynamic equilibrium. Thin film is characterized for amorphous nature by using X-ray diffraction technique (Model: Philips PW1610, Goniometer: Philips 1710, detector: Cu K_α). The absence of any prominent peaks, confirmed the amorphous nature of thin film.

The photoconductivity of the amorphous film has been studied by mounting it in a specially designed metallic sample holder where heat filtered white light (200 W Tungsten lamp) can be shone through a transparent quartz window. A vacuum of about 10^{-3} mbar is maintained throughout these measurements. Light intensity is measured by a digital Luxmeter (Testron, model TES-1332). The photocurrent is obtained after subtracting dark current from the current measured in presence of light. For transient photoconductivity measurements, light is shone on the thin film and the rise of photocurrent is noted manually from a digital picoammeter (DPM-111 Model). The accuracy in I_{ph} measurements is typically 1pA. I-V curves are symmetric and linear upto 30 V in the dark.

3. Results and discussion

Fig. 1 shows the temperature dependence of dark conductivity (σ_d) and photoconductivity (σ_{ph}) for the thin films of a-$(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$. The plot of $\ln\sigma_d$ vs. $1000/T$ is straight line indicating that conduction is an activated process having single activation energy in the temperature range 283–350 K. The σ_d can, therefore, be expressed by the usual relation

$$\sigma_d = \sigma_o \exp\left(\frac{-\Delta E}{kT}\right) \tag{1}$$

where ΔE is the activation energy for dc conduction and k is the Boltzmann's constant. The values of ΔE and σ_d are calculated from the slope of the curve of Fig. 1 and are found to be (0.80 ± 0.01) eV and $(2.00 \pm 0.05) \times 10^{-8}$ $\Omega^{-1}cm^{-1}$ at 297 K respectively. Fig. 1 also contains the plot of σ_{ph} vs. $1000/T$. It is clear from the figure that the photoconductivity is an activated process and the activation energy (ΔE_{ph}) for photoconduction is much smaller than dark conduction. The values of ΔE_{ph} and σ_{ph} are calculated from the slope of the curve of Fig. 1 and are found to be (0.48 ± 0.01) eV and $(1.97 \pm 0.01) \times 10^{-7}$ $\Omega^{-1}cm^{-1}$ at 297 K respectively. It is also clear from the figure that no maximum in the steady state photoconductivity with temperature has been observed in the measured temperature range. Similar results have been reported [15, 16] in various other chalcogenide glasses also. A maximum in the photoconductivity is a general feature of chalcogenide glasses and various theories [16–19] have been put forward to explain the maximum.

Intensity dependence of steady state photoconductivity has also been studied to see the nature of recombination processes. The plots of $\ln\sigma_{ph}$ vs. lnF are straight lines at all temperatures as shown in Fig. 2, which indicate that the photoconductivity (σ_{ph}) follows a power law with intensity (F) i.e.

$$\sigma_{ph} \propto F^{\gamma} \tag{2}$$

where $0.5 \le \gamma \le 1.0$. According to Rose [20] the value of γ between 0.5 and 1.0 can not be understood by assuming a set of discrete trap levels but considering the existence of continuous distributions of trap levels in the band gap. In a-$(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ thin film also, the value of γ lies between 0.5 and 1.0 which indicate that a continuous distribution of localized states exists in the mobility gap and the resulting recombination mechanism will be bimolecular [21], where the recombination rate of electrons is proportional to the number of holes. In non-equilibrium condition, most of the electrons and holes are generated after shining light and are located at D° centres. These centres decrease by recombination process [$2D^\circ \mapsto D^+ + D^-$] when the illumination is stopped [21].

Fig. 3 shows the rise and decay of photocurrent at different temperatures. It is clear from the figure that the photocurrent rises monotonically to the steady state value and the decay of photocurrent is quite slow. A

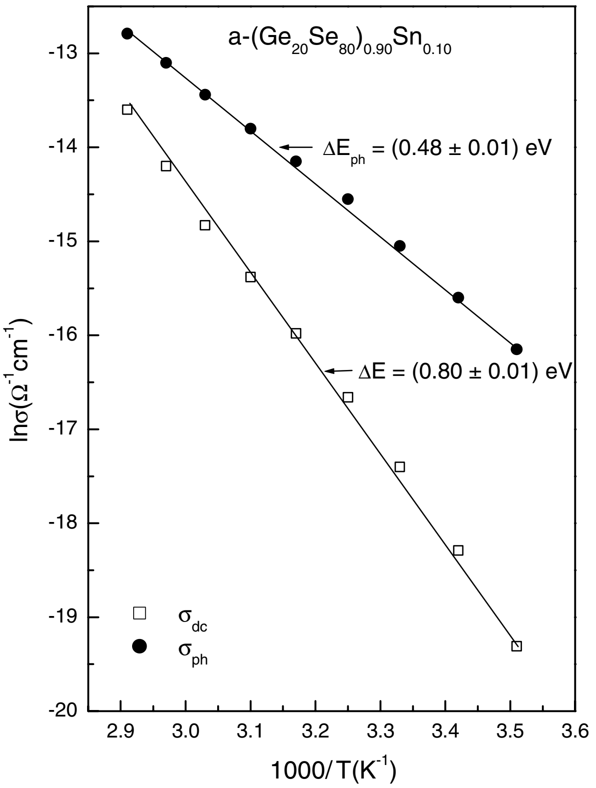

Figure 1 Temperature dependence of dark (σ_d) and photo conductivity (σ_{ph}).

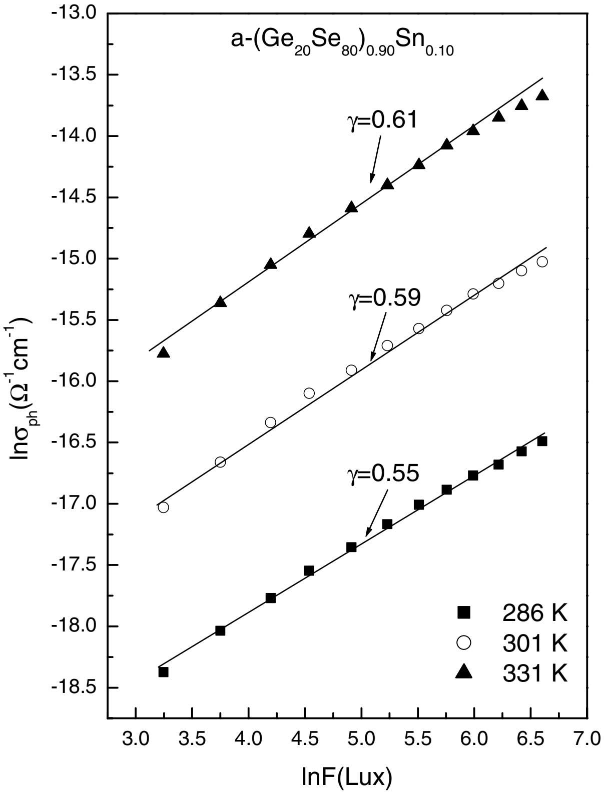

Figure 2 Intensity dependence of photoconductivity (σ_{ph}) at different temperatures.

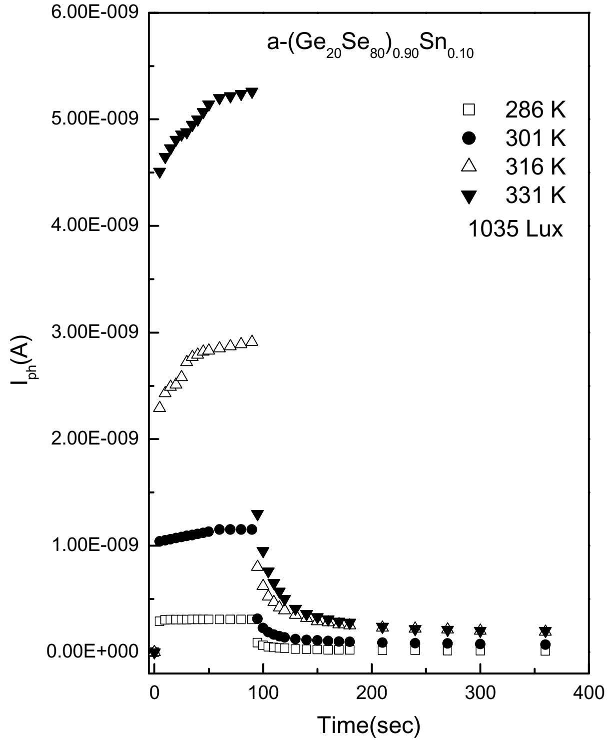

Figure 3 Rise and decay of photocurrent (I_{ph}) at different temperatures.

persistent photocurrent is observed at all temperatures, which is a common feature of other chalcogenide glasses [22, 23]. Fig. 4 shows the rise and decay of photocurrent at different intensities at 286 K. It is clear from the figure that the decay of photocurrent is quite slow at all intensities.

From above observations, it is clear that the persistent photocurrent is observed at all temperatures and intensities and it is believed that the persistent photocurrent may not be simply due to carriers trapped in the localized states [22]. So, for simplifying the analysis, the persistent photocurrent is subtracted from the measured photocurrent. Figs. 5 and 6 show the plots between lnIph vs. time curves at different temperatures and different intensities respectively. These curves must be straight lines in case of single trap level. However, in the present case, these curves are not having same slope but the slope goes on decreasing continuously as the time of decay increases. This indicates that the traps are present at all the energies in the band gap. These traps have different time constant and hence giving the non-exponential decay of photoconductivity at all temperatures and intensities. In amorphous materials, having traps in the mobility gap, the recombination time of carriers is same as the carrier life time when the free carrier density is more than the trapped carrier density [23]. If the free carrier density is much less than the trapped carriers, then the recombination process is dominated by the rate of trap emptying and is much larger than the carrier life time, resulting in a slow decay.

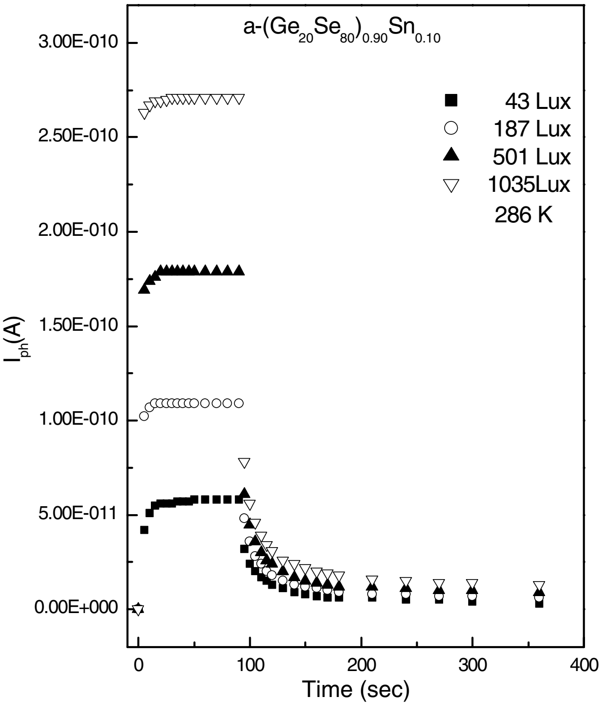

Figure 4 Rise and decay of photocurrent (I_{ph}) at different intensities.

To study the decay rate analysis quantitatively at various temperatures and intensities the decay time constant [24] has been calculated using relation:

$$\tau_d = -\left[\frac{1}{I_{ph}}\left(\frac{dI_{ph}}{dt}\right)\right]^{-1} \tag{3}$$

From the slope of I_{ph} vs time curves (result not shown here), we have calculated the values of τ_d using Equation 3 at various times of the decay curves of Figs. 3 and 4. Fig. 7 shows the plot of τ_d vs. time at a temperature 286 K and at intensity 1035 Lux. It is clear from the figure that the decay constant increases with time, which confirms the non-exponential decay of photocurrent. For exponential decay, the decay constant should not vary with time. Fig. 8 shows the plot of τ_d vs. intensity at a particular time ($t =$ 15 s). It is clear from figure that the value of τ_d increases with intensity. The results are similar at other temperatures also (results not shown here).

According to Fuhs and Meyer [24], the recombination with in the localized states is considered to be the predominant recombination mechanism at all temperatures and intensities. When I_{ph} increases with temperature, the excess charge carrier density is given by

$$\Delta p = \frac{N_v}{N}\sqrt{\frac{g_o}{a_1}}\exp\left[-\frac{E_{tp}}{kT}\right] \tag{4}$$

where N = concentration of hole traps (in this case); N_v= density of states in the valence band; E_{tp}= energetic depth of hole traps; g_o= excess carrier generation rate; a_1= recombination rate.

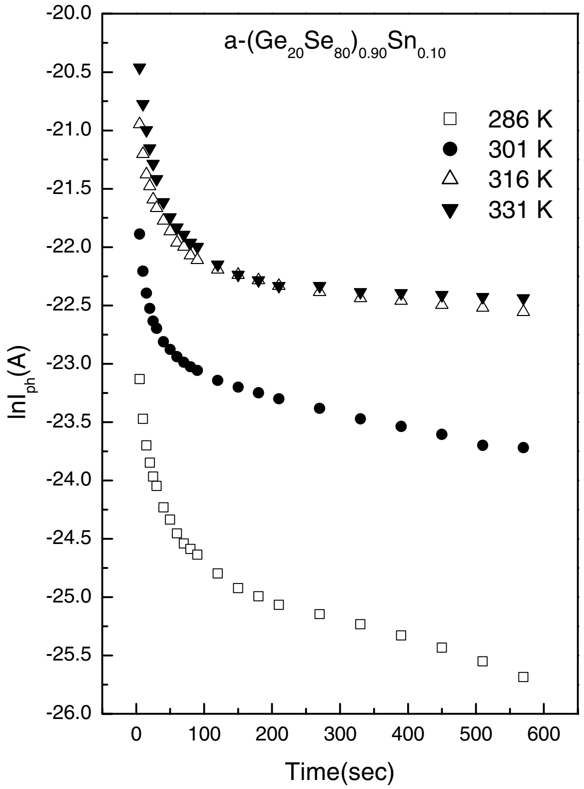

Figure 5 Time dependence of photocurrent at different temperatures during decay.

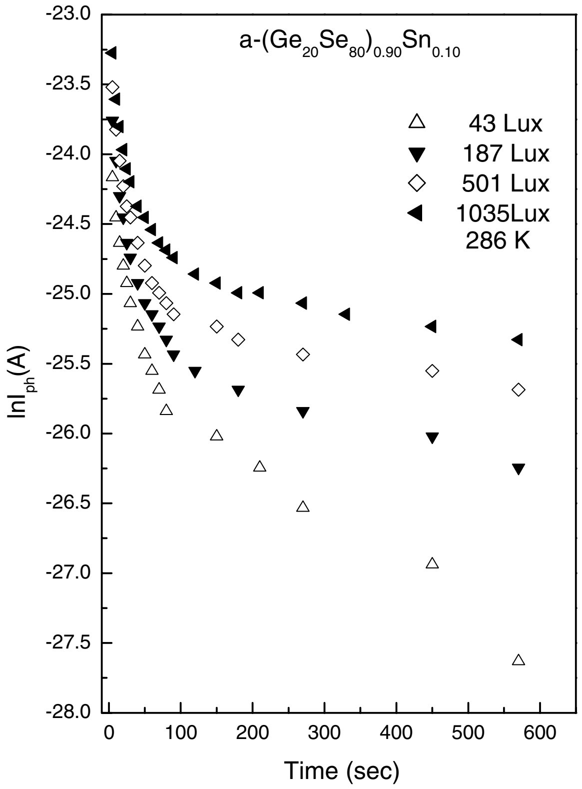

Figure 6 Time dependence of photocurrent at different intensities during decay.

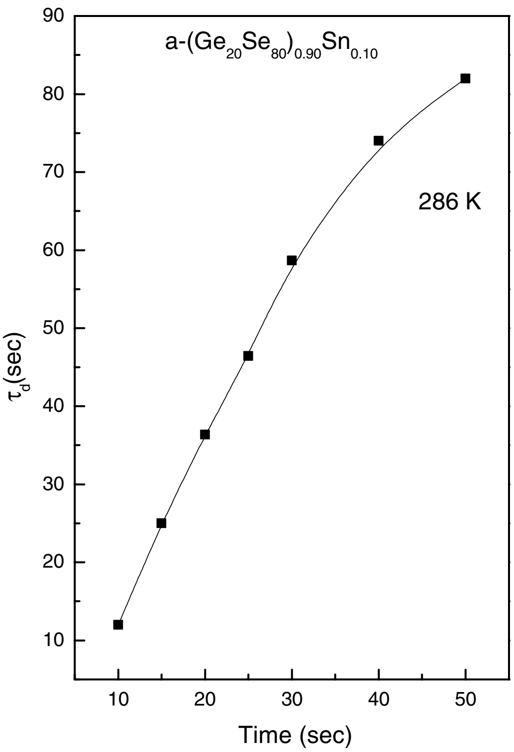

Figure 7 Variation of differential life time constant (τ_d) with time.

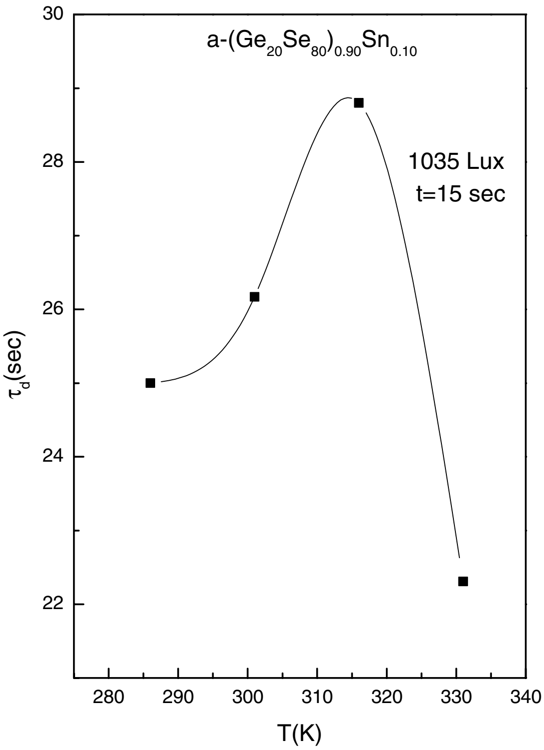

Figure 9 Temperature dependence of differential life time constant (τ_d).

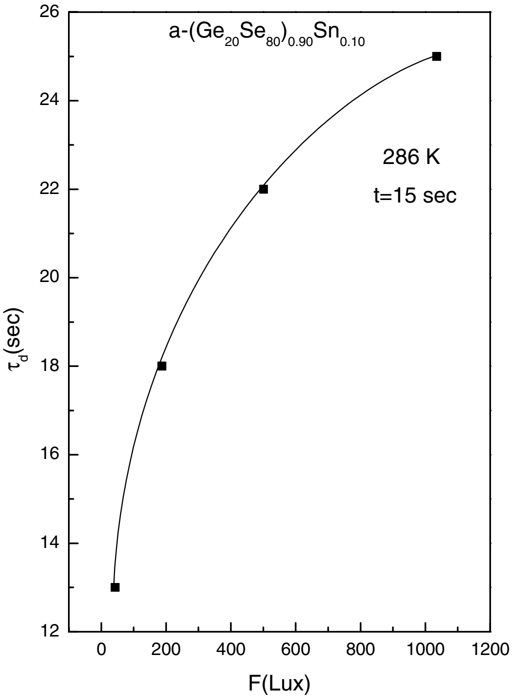

Figure 8 Intensity dependence of differential life time constant (τ_d).

From Equation 4 it is clear that steady state photoconductivity should increase exponentially with temperature and square root of intensity. In this case also, the authors have observed the same type of behaviour. Fuhs and Meyer [24] have also shown that

$$\frac{\Delta p(t)}{\Delta p(0)} = \frac{1}{\left(1 + \frac{t}{\tau_d}\right)} \tag{5}$$

$$\text{where} \qquad \tau_d = \sqrt{a_1 g_o} \tag{6}$$

From Equation 6, it is clear that the decay constant (τ_d) should increase with the intensity of illumination. In the present case also τ_d increases with the intensity of illumination (see Fig. 8).

The temperature dependence of τ_d has been calculated using Equation 3 at a fixed time $t = 15$ sec. Fig. 9 shows the plot between τ_d and temperature at a particular intensity 1035 Lux for a-$(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$ thin film. It is clear from the figure that the value of τ_d first increases and then decreases after a certain temperature. The decrease in the value of τ_d with increasing temperature is probably due to an increase in the number of thermally generated trap centres. This type of behaviour of τ_d has also been reported by Moustakas *et al.* [25] and Main *et al.* [26]. This behaviour has been attributed to the presence of gap states near the mobility edge. In the presence of these gap states, the calculated τ_d will be longer than the decay time of mobile carriers, if the carriers recombine via these states.

4. Conclusions

Temperature dependence of dark conductivity and photoconductivity is studied in amorphous thin films of $(Ge_{20}Se_{80})_{0.90}Sn_{0.10}$, prepared by vacuum evaporation technique. Temperature dependence of photoconductivity measurements indicate that photoconductivity is also thermally activated process in the measured temperature range. Transient photoconductivity measurements at different intensities and temperatures indicate that the photocurrent is initially decays very fast and later on becomes very slow. This decay is found to be non-exponential indicating the presence of continuous distribution of defect states. The present results can be understood if the recombination is taking place within the localized states.

Acknowledgments

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