

EFFECT OF THERMAL ANNEALING ON THE ELECTRICAL PROPERTIES OF AMORPHOUS $\text{Se}_{75}\text{Te}_{15}\text{Sn}_{10}$ THIN FILMS

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The present paper reports the steady state and transient photoconductivity measurements in vacuum evaporated $\text{Se}_{75}\text{Te}_{15}\text{Sn}_{10}$ thin films before and after thermal crystallization which is induced by thermal annealing. The results indicate that the dark conductivity (σ_d) and steady state photoconductivity (σ_{ph}) increase by several orders of magnitude on crystallization. Photosensitivity (I_{ph} / I_d) also changes by a factor of 1.6×10^3 . The transient behaviour is also affected quite appreciably. The results are interpreted in terms of the defect states present in the material.

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1. Introduction

In recent years, chalcogenide thin films have become a subject of systematic research because of the changes in physico-chemical properties which are caused due to thermal annealing [1-3]. These thermally induced effects may be either reversible or irreversible, and offer the possibility of using amorphous chalcogenide semiconductors for high density optical recording [4,5]. In particular, Se-Te alloys are very attractive candidates for all these technological applications. The common feature of these glasses is the presence of localized states in the mobility gap due to absence of long range order as well as various inherent defect states. Photoconductivity measurements in chalcogenide thin films are important from basic as well as an applied scientific point of view. These measurements may be useful in understanding the recombination mechanism which in turn gives information regarding localized states in the mobility gap of these materials. In chalcogenide semiconductors, recombination centers are the defects with negative effective correlation energy (negative U-model [6]). These defects produce discrete energy levels in the gap of amorphous chalcogenide semiconductors [7]. Se-Te alloys have gained much importance because of their higher photosensitivity, greater hardness, higher crystallization temperature, and smaller ageing effects as compared to the pure Se glass. The addition of third element into Se-Te alloys expands the glass forming region and also creates compositional and configurational disorder in the system. The lattice perfection and the optical gap of the material play a major role in the preparation of the device which can be modified by the addition of the dopant (Sn). Therefore, the photoconducting properties of $\text{Se}_{75}\text{Te}_{15}\text{Sn}_{10}$ alloy are interesting to study in detail. The effect of thermal annealing is also quite important as this alloy has very small crystallisation temperature (T_c). The effect of crystallization on dc conductivity has also been studied in detail by many workers [8,9]. However, no such systematic efforts have been made to study the effect of thermal annealing on photoconductive behaviour of amorphous $\text{Se}_{75}\text{Te}_{15}\text{Sn}_{10}$ thin films.

In view of the above, we have studied the effect of thermal annealing on steady state and transient photoconductivity in vacuum evaporated thin films of $\text{Se}_{75}\text{Te}_{15}\text{Sn}_{10}$ as a function of temperature (300 K to 337 K) and intensity (3 Lux to 1035 Lux). The annealing was done at a particular temperature (337 K) for 4815 minutes in vacuum ($\approx 10^{-3}$ mbar). The measurements have been done in two states (i) the films annealed at temperature 330 K (state A), (ii) the films annealed at

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337 K (state B). Our transient photoconductivity measurements show that the behaviour of rise and decay curves is quite different in the two states.

Section 2 describes the experimental details of sample preparation and photoconductivity measurements. The results are presented and discussed in section 3. The last section deals with the conclusions drawn from the present work.

2. Experimental

Glassy alloy of $\text{Se}_{75}\text{Te}_{15}\text{Sn}_{10}$ was prepared by quenching technique. Materials (99.999% pure) were weighed according to their atomic percentage and sealed in quartz ampoule in a vacuum $\sim 2 \times 10^{-5}$ mbar. The sealed ampoule was kept inside a furnace where the temperature was increased upto 1025 K at a heating rate of 2-3 °C/min. The ampoule was frequently rocked for 24 hours at the highest temperature to make the melt homogeneous. The quenching was done in L N_2 . Thin film of the alloy was prepared by vacuum evaporation technique keeping substrate at room temperature and base pressure of $\sim 2 \times 10^{-5}$ mbar using a molybdenum boat. Pre-deposited thick indium electrodes on well degassed corning 7059 glass substrates were used for the electrical contacts. A planar geometry of the film (length ~ 1.78 cm; electrode gap $\sim 8 \times 10^{-2}$ cm) was used for electrical measurements. The thickness of the film was about 5000 Å. The film was kept in the deposition chamber in dark for 24 hrs before mounting in the metallic sample holder to attain thermodynamic equilibrium as stressed by Abkowitz et al. [10].

The photoconductivity of the amorphous film was studied by mounting in a specially designed metallic sample holder where heat filtered white light (200 W tungsten lamp) could be shone through a transparent quartz window. A vacuum of about 10^{-3} mbar was maintained throughout these measurements. The results were found to be the same in higher vacuum $\sim 10^{-5}$ mbar also which we had verified in our laboratory. Light intensity was measured by a digital Luxmeter (Testron, model TES-1332). The photocurrent (I_{ph}) was obtained after subtracting dark current (I_{d}) from the current measured in the presence of light. For measurement of transient photoconductivity, light was shone on the sample and rise of photocurrent was noted manually from a digital picoammeter (DPM-111 Model). The accuracy in I_{ph} measurements was typically 1 pA. First of all the films were annealed at 330 K for 2 hrs in a vacuum of about 10^{-3} mbar and the dark conductivity and photoconductivity measurements were carried out. Then the films were annealed at a temperature of 337 K for 4815 minutes and the same measurements were performed after thermal annealing treatment (state B).

3. Results and discussions

3.1 Dark conductivity measurements

Fig. 1 shows the temperature dependence of dark conductivity (σ_{d}) in thin films of $\text{Se}_{75}\text{Te}_{15}\text{Sn}_{10}$ in both states (A & B). Curves of $\ln \sigma_{\text{d}}$ vs $1000/T$ have been found to be straight lines after each annealing time which indicates a thermally activated process for dc conduction (σ_{d}). σ_{d} can, therefore, be expressed by a usual relation:

$$\sigma_{\text{d}} = \sigma_0 \exp(-\Delta E_{\text{d}} / kT) \quad (1)$$

where ΔE_{d} is the activation energy for dc conduction and k is the Boltzmann constant.

The values of ΔE_{d} were calculated for both the states using the slope of the curves of Fig. 1 and are inserted in Table 1, which also contains the values of σ_{d} at 305 K for both states A & B. It is clear from the table that the value of ΔE_{d} decreases from 0.94 eV to 0.33 eV and σ_{d} increases from $4.82 \times 10^{-11} \Omega^{-1}\text{cm}^{-1}$ to $2.37 \times 10^{-5} \Omega^{-1}\text{cm}^{-1}$ after annealing the films at 337 K for 4815 min. Our X-ray diffraction curves show some crystalline peaks in the state B. This is quite likely due to partial crystallization of the amorphous film after annealing at this temperature for so long time.

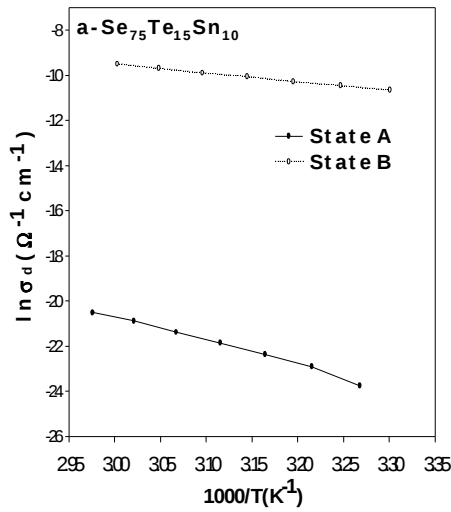


Fig. 1. Temperature dependence of dark conductivity in state A and B.

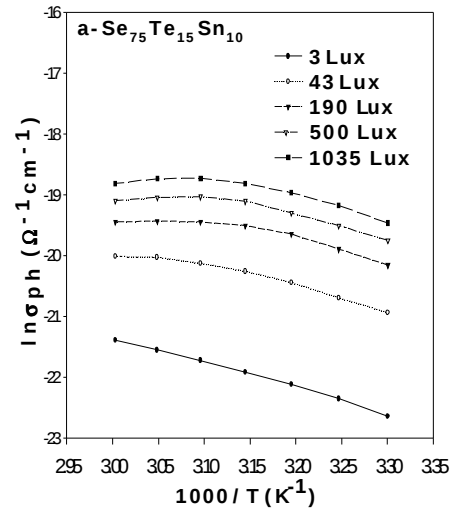


Fig. 2. Temperature dependence of steady state photoconductivity in state A.

Table 1.

Parameters	State A	State B
$\sigma_d (\Omega^{-1}\text{cm}^{-1})$	4.82×10^{-11}	2.37×10^{-5}
ΔE (eV)	0.94	0.33
$\sigma_{ph} (\Omega^{-1}\text{cm}^{-1})$	3.52×10^{-9}	3.17×10^{-6}
ΔE_{ph} (eV)	0.13	0.30
σ_{ph} / σ_d	160	0.1
γ	0.5	0.5
τ_d	3.1	10.3

3.2 Steady state photoconductivity

Figs. 2 and 3 show the temperature dependence of steady state photoconductivity at various levels of illumination in states A and B. It is clear from these figures that σ_{ph} increases exponentially in the temperature range 300 K to 337 K. The activation energy of photoconduction (ΔE_{ph}) is much smaller than that of dark conduction and is almost independent of the intensity of light used. The values of ΔE_{ph} and σ_{ph} at 305 K are inserted in the table. At higher temperatures a maximum in the photoconductivity is observed in state A whereas this maximum is absent in state B, which is a common feature of chalcogenide glasses. According to Mott and Davis [11], a maximum is observed when $I_{ph} \gg I_d$ and this is absent when $I_{ph} \ll I_d$. In our case also, a maximum is observed in state A where $I_{ph} \gg I_d$ ($I_{ph} / I_d \approx 160$) and this maximum is absent in state B where $I_{ph} \ll I_d$ ($I_{ph} / I_d \approx 0.1$). The increase in σ_{ph} after annealing (state B) indicates that the material is becoming more photoconducting in absolute physical terms. In general,

$$\sigma_{ph} \sim (\text{carrier mobility}) \times (\text{life time}) \quad (2)$$

The increase in σ_{ph} may be related to the increase in carrier mobility due to partial crystallization. However, the band gap and optical absorption coefficient may also change during the crystallization. The structural changes are also quite likely upon crystallization which influences the

grain boundaries and tissue structure of the material. In the absence of knowledge of these details, the exact reason for increase in σ_{ph} upon thermal annealing can not be predicted. The intensity dependence of steady state photoconductivity has also been studied in both the states A and B (results are not shown here, but the values are inserted in the table). It is clear from the measurements that, in both states, the photoconductivity grows linearly with light intensity (over three orders of magnitudes) and, therefore, photo carrier generation rate G , follows the relation $I_{ph} \propto G^\gamma$, where power γ lies between $0.5 \leq \gamma \leq 1.0$. $\gamma \approx 1$ means monomolecular recombination and $\gamma \approx 0.5$ means bimolecular recombination behaviour. Between these two extreme cases, there are intermediate values for γ between 0.5 and 1.0. In the present case, $\gamma \approx 0.5$ in both states indicates the continuous distribution of localized states that exist in the mobility gap of the present material.

These results can be explained on the basis of the model proposed by Main and Owen [12] and Simmons and Taylor [13]. This model provides the information for the energy location of discrete sets of localized states in the gap. The concept of charged coordination defects with negative-U could be responsible for such states [14,15]. The D^+ and D^- centers can act as discrete traps for photo-generated electrons and holes, thereby giving rise to neutral D^0 sites which, due to polaronic lattice deformation, produce energy levels roughly midway between the band edges and the Fermi level.

Photosensitivity (σ_{ph}/σ_d) is an important parameter in photoconductivity measurements which determines the use of a particular material for solar cells etc.. The decrease in σ_{ph}/σ_d on partial crystallization may be due to increase in dark conductivity. However, our transient photoconductivity measurements (discussed later) show that the density of states may increase after annealing at 337 K for 4815 minutes (state B). The increase or decrease in the defect density will also result in decrease or increase in photosensitivity respectively.

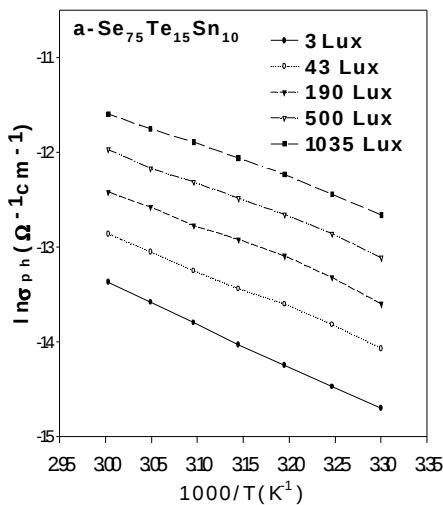


Fig. 3. Temperature dependence of steady state photoconductivity in state B.

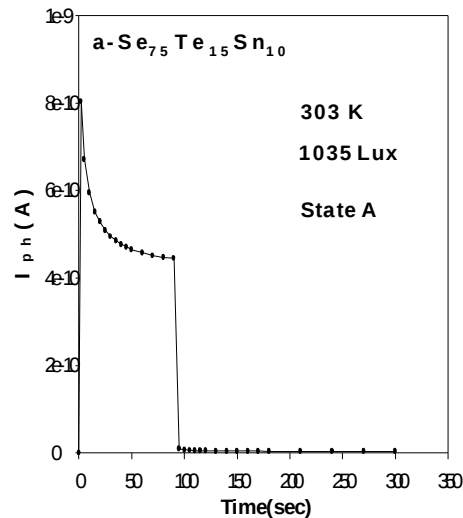


Fig. 4. Rise and decay of I_{ph} in state A.

3.3 Transient photoconductivity

Fig. 4 and 5 show the rise and decay of photocurrent at room temperature and intensity of 1035 Lux for both the states. It is clear from figures that the rise and decay curves changed quite appreciably after annealing at 337 K for 4815 min (state B). A peak in the increasing part of curve is observed in state A and the decay is quite fast. This anomalous behaviour in the rise curve was also observed by other workers and explained in terms of non-equilibrium recombination as suggested by Andriesh et al. [15]. According to them, such a maximum occurs in high intensity region where bimolecular recombination takes place. At lower intensities, where monomolecular recombination takes place, this maximum may be absent and photocurrent increases monotonically to the steady state. Iovu et al. [16] have also found a similar maximum in Sn doped $a\text{-As}_2\text{Se}_3$ and AsSe films. According to them, at short times, $t < t_R$ (time at which the transition from recombination free to

molecular recombination controlled photocurrent occurs), recombination is not yet significant and the rise of photocurrent is fully controlled by carrier trapping, yielding

$$I_{ph} \approx G t^\alpha \quad (3)$$

where G is the generate rate and α is the dispersion parameter. At longer times, photocurrent rise depends on the excitation intensity.

At low intensities, recombination is always dominated by monomolecular recombination, the photocurrent increases monotonically and saturates at a steady state value. At higher intensities, a quasistationary portion of the photocurrent is obtained after saturation, followed by a decreasing portion of the transient curve which is governed by the equation:

$$I_{ph} \approx G^{1/2} t^{-(1-\alpha)/2} \quad (4)$$

Here the bimolecular recombination is dominant over monomolecular recombination. At even higher excitation levels, the rise is entirely controlled by the bimolecular recombination and the quasistationary portion of the photocurrent is absent. In such cases, the photocurrent exhibits an overshoot. According to Kastner et al. [17] and Arkhipov et al. [18], this overshoot in the photocurrent transient, which in terms of the multiple trapping model, is due to non-equilibrium bimolecular recombination whose intensity increases with the total carrier density. If this recombination mode is dominant, the rate of recombination sooner or later gets high enough and, together with carrier trapping by states below the demarcation level, provides conditions for decreasing the density of free carriers. Maan et al. [19] have also found a similar maximum in $\text{a-In}_{20}\text{Se}_{80}$ and the rise of photocurrent during illumination has been attributed to recombination between holes in valence band with electrons at recombination centers. The possibility of light induced defects as a possible cause for such a behavior may also not be ruled out.

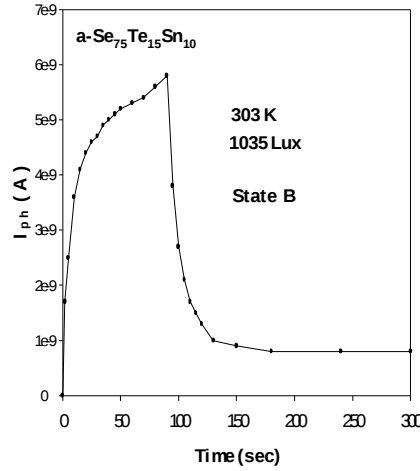


Fig. 5. Rise and decay of I_{ph} in state B.

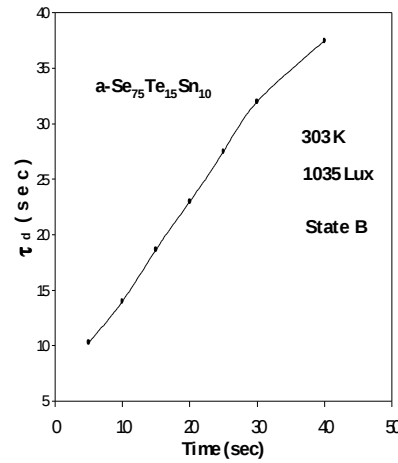


Fig. 6. τ_d as a function of time during decay of photocurrent in state B.

It is interesting to note that such a maximum in the rise of photocurrent disappears in the crystallized state (state B). This indicates that anomalous behavior of the rise in photocurrent may be the characteristic of amorphous state. The decay of photocurrent in state B is quite slow. A persistent photocurrent (the asymptotic value of the photocurrent in the decay curve) is also observed in this state. The persistent photocurrent is observed in many chalcogenide glasses [20].

According to Igalson [20], the persistent photocurrent may not be simply due to the carriers trapped in the localized states. To simplify the analysis, we subtracted the persistent photocurrent from the measured photocurrent and found that the decay of photocurrent is non-exponential even after subtracting the persistent photocurrent. In discussing the non-exponential decay process, we prefer to use the concept of differential life time as suggested by Fuhs and Meyer [21]. According to these workers, the differential life time can be expressed as

$$\tau_d = - [(1/I_{ph}) (dI_{ph} / dt)]^{-1} \quad (5)$$

The values of τ_d are calculated at various times using slopes of I_{ph} vs. time curves and eqn (5). The corrected values of I_{ph} are used for these calculations. The results (state B) have been plotted in Fig. 6. It is clear from this figure that τ_d increases with the increase of time which confirms that the decay is non-exponential in this case. However, for an exponential decay, τ_d should be constant with time. It is also clear from the table that the value of τ_d at a particular time ($t = 5$ sec) is more in state B as compared to state A. This indicates that the decay of photocurrent becomes slower after thermal annealing. A slower decay of photocurrent in state B indicates that the density of defect states increases after thermal annealing in the present case.

4. Conclusions

Steady state and transient photoconductivity measurements have been performed in amorphous thin film of $Se_{75}Te_{15}Sn_{10}$ at various temperatures and intensities in the two states A and B. σ_d and σ_{ph} increases in state B as compared to state A. σ_{ph} / σ_d decreases quite appreciably in state B. The transient behavior is also affected drastically in state B as compared to state A. A slower decay of photocurrent in state B is caused due to enhanced carrier trapping by more number of defect states which are apparently created due to thermal annealing. A decrease in photosensitivity and the absence of maximum in the rise of photocurrent can also be understood due to the enhanced trapping by a higher number of defect states.

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