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Photoconductivity of $Se_{90-x}Te_{10}Zn_x$ thin films

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Photoconductive properties such as dark conductivity, steady state and transient photoconductivity of a-$Se_{90-x}Te_{10}Zn_x$ thin films, prepared by thermal vacuum evaporation technique have been studied in temperature range 312-380 K. Analysis of data shows that activation energy of dark current is greater as compared to activation energy of photo current. Activation energy decreases with increase in Zn concentration which may be due to increase in defect density of states. Analysis of intensity dependent photoconductivity shows that bimolecular recombination is predominant. Photosensitivity is found to be maximum for $Se_{88}Te_{10}Zn_2$ composition after that it decreases with increase in Zn concentration. Carrier lifetime decreases with increase in Zn concentration which also confirms that density of defect states increases. Transient photoconductivity shows that the carrier lifetime decreases with increase in Zn concentration. This decrease is due to transition trapping process.

Keywords: Photoconductivity, *dc* Conductivity, Chalcogenides, Photosensitivity, Activation energy

1 Introduction

Chalcogenide glasses are inorganic glassy materials which contain one or more chalcogens S, Se or Te. These materials have high refractive index (ranging 2.0 to 3.5), highly transparent to IR-radiations and their band gap lies in the sub-band gap[1,2]. Due to lack of periodicity and inherent defects, these materials have large number of localized states in mobility gap. These impurity effects are also important for fabrication of many optical devices and optical data storage[3]. These are most promising materials for optical applications like optical limiting, anti-reflection coating, solar cells, thermal imaging, tunable lasers, optical rewritable data storage media, infrared power delivery, optoelectronic devices, IR emitter, manufacture of filters, IR detector[4-7], etc. Chalcogenide glasses exhibit light induced effects. Bonding configuration and structure of chalcogenide glasses change with the incidence of light which is reversible sometimes. This is due to rapid localization of photo-excited carriers. Photoconductivity yields information about the defects and metastable structural states. These defects produce discrete energy levels in the gap of chalcogenide glasses[8]. Due to photoconductivity measurements, the position of these discrete energy levels can be identified. Dependence of photocurrent on intensity of illumination and temperature allows the identification of areas with monomolecular or bimolecular recombination. At low light intensity and high temperature monomolecular recombination dominates, but at high light intensity and low temperature bimolecular recombination leads. Transient photoconductivity measurements are important because rise and decay of photocurrent with time show the presence of traps in the mobility gap in materials. These traps originate from defect states, present in materials. Transient photoconductivity measurements give information about the localized states in these materials. Transient photoconductivity measurements have been reported earlier by various researchers[9-14]. Many researchers reported impurity effects in chalcogenide glasses[15-17]. Amorphous Se rich semiconducting alloys are used as photoconductors in high definition television camera tubes and X-ray imaging. Structure of a-Se has two fold co-ordinations, consists of long polymeric Se_n Chains. In Se-Te alloys, Te enters in structure by isoelectronic substitution. Te addition changes the inter chain Vander Waal's bonding because atomic size of Te is larger than Se. Se-Te alloys have much importance because of their superiority over amorphous Se. Addition of Te in Se chain reduces the electronic band gap of Se to make it useful in a photoreceptor having desirable spectral response for xerographic purposes[18]. Addition of a third element creates configurationally and compositional disorder in system. In the present paper, steady state and transient photoconductive properties of $Se_{90-x}Te_{10}Zn_x$ have been studied.

2 Experimental Details

Melt quenching technique has been used for preparing bulk samples of $Se_{90-x}Te_{10}Zn_x$ (x = 0, 2, 5, 10). Initially, composition of selenium, tellurium and zinc has been taken according to their atomic percentage. Weighted materials have been introduced into quartz ampoules evacuated at a pressure of 10^{-5} torr and then sealed. Sealed ampoules have been placed inside the furnace at 1100 K temperature for 12 h. Ampoules have been rotated continuously for homogeneous mixing of composition. After heating in furnace, ampoules have been quenched in ice cool water. Fast cooling of melt composition enables to obtain the glassy materials. Glass slides used as substrate have been cleaned by ultrasonic bath and acetone. Thermal evaporation technique has been used for making thin films of the material (under a pressure of 10^{-5} torr) on glass substrate at room temperature. Thickness of films has been measured 300 nm by single crystal thickness monitor. Pre-deposited indium electrodes on substrate have been used for electrical contacts. Dark and photo conductivity measurements of amorphous films have been studied in the temperature range 312-380 K by mounting it in a specially designed metallic sample holder in which white light (200 W tungsten lamp) can be shown through a window. Increase in temperature by the lamp was 4-6 K and at this temperature thermal effects are not predominate. Transient photoconductivity has been measured at 3650 lux for all compositions. Dark current is subtracted from total current to obtain photocurrent. XRD patterns of films have not shown any peak which confirms the amorphous nature of the films as shown in Fig. 1. Chemical composition of $Se_{90-x}Te_{10}Zn_x$ thin films have been determined using energy dispersive X-ray analysis. Intensity of light has been measured by a digital Luxmeter (MS6610).

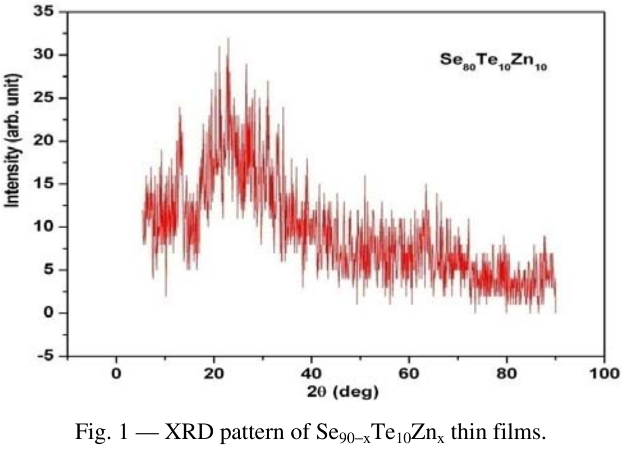

Fig. 1 — XRD pattern of $Se_{90-x}Te_{10}Zn_x$ thin films.

3 Results

Effect of Zn concentration on electrical conductivity (σ_{dc}) in $Se_{90-x}Te_{10}Zn_x$ thin films has been studied. The *dc* conductivity (σ_{dc}) is calculated during heating (312-380 K) at constant voltage of 1.5 V. Figure 2 shows temperature dependent *dc* conductivity (σ_{dc}) of $Se_{90-x}Te_{10}Zn_x$ thin films. Plots of $\ln\sigma_{dc}$ versus $1000/T$ are found to be straight lines. This shows that conduction is through an activated process. For semiconducting glasses, *dc* conductivity can be expressed by Arrhenius relation:

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-\Delta E_{dc}}{kT}\right) \qquad \ldots(1)$$

where ΔE_{dc} is activation energy, σ_0 is pre-exponential factor related to the material, k is known as Boltzmann constant and T is temperature. Activation energy (ΔE_{dc}) is estimated by the slope of $\ln\sigma_{dc}$ versus $1000/T$ and using Eq. (1). Slope of the curve is estimated by using linear fit. Values of activation energy (ΔE_{dc}), *dc* conductivity (σ_{dc}) and pre-exponential factor (σ_0) are given in Table 1. Composition dependent *dc* conductivity is studied and it is observed that *dc* conductivity increases and activation energy (ΔE_{dc}) decreases with Zn concentration as shown in Fig. 3. Dark *dc* conductivity and photoconductivity increase exponentially with increase in temperature, which shows that conduction is through thermally activated process. This shows that these alloys have semiconducting behaviour.

Conduction process also depends on the value of pre-exponential factor σ_0. For extended state conduction, value of σ_0 is high and for hopping conduction in localized states, value of σ_0 is very

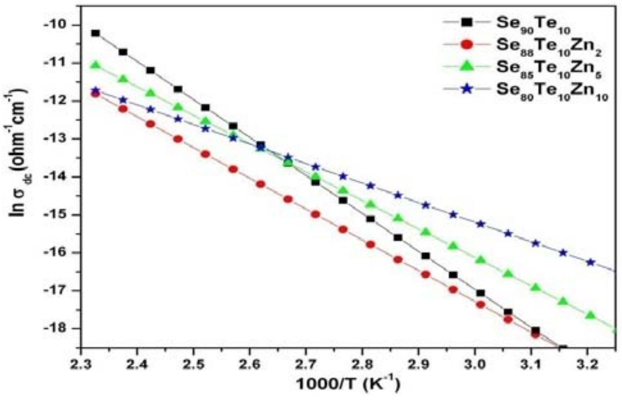

Fig. 2 — Temperature dependent *dc* conductivity in $Se_{90-x}Te_{10}Zn_x$ thin films

small. In the present case, value of σ_0 is (10^1-10^5 Scm^{-1}) so the conduction is due to extended state conduction. Fig. 4 shows steady state photoconductivity (σ_{ph}) of $Se_{90-x}Te_{10}Zn_x$ thin films with temperature at intensity (3650 lux). Activation energy (ΔE_{ph}) value is calculated by using slope of Fig. 4 as given in Table 1. From Fig. 4, it is clear that photoconductivity is an activated process and activation energy of dark current is larger than photocurrent. Reason is that the measurement of conductivity of the sample is taken in the intermediate temperature range. According to theory, temperature dependent steady state photoconductivity curve in amorphous semiconductors[19-21] shows three regimes:

(1) At low temperature, σ_{ph} is directly proportional to light intensity and nearly constant with temperature or in other words the photoconductivity is directly proportional to generation rate '*g*'.

(2) At intermediate temperature, photoconductivity (σ_{ph}) is a sub linear function of light intensity and rises with temperature. In this case, rate of recombination is governed by photo-generated carriers and σ_{ph} is directly proportional to g^{γ} and is less than σ_{dc}.

Table 1 — Variation of activation energy (ΔE_{dc}, ΔE_{ph}), *dc* conductivity (σ_{dc}, σ_{ph}) and pre-exponential factor (σ_o) in dark and light with the change in Zn concentration of $Se_{90-x}Te_{10}Zn_x$ thin films in temperature range (312-380 K)

Sample	ΔE_{dc} (eV)	σ_{dc} ($\Omega^{-1}cm^{-1}$)	σ_o ($\Omega^{-1}cm^{-1}$)	ΔE_{ph} (eV)	σ_{ph} ($\Omega^{-1}cm^{-1}$)
$Se_{90}Te_{10}$	0.86	3.28×10^{-8}	3.86×10^{5}	0.34	2.336×10^{-8}
$Se_{88}Te_{10}Zn_2$	0.70	4.45×10^{-8}	1.94×10^{3}	0.33	4.45×10^{-8}
$Se_{85}Te_{10}Zn_5$	0.65	1.13×10^{-7}	8.6×10^{2}	0.29	7.52×10^{-8}
$Se_{80}Te_{10}Zn_{10}$	0.44	2.27×10^{-7}	1.10	0.23	11.48×10^{-8}

(3) At high temperature, dark conductivity (σ_{dc}) is greater than photoconductivity (σ_{ph}), photoconductivity (σ_{ph}) decreases with increase in temperature and is proportional to intensity (σ_{ph} is directly proportional to '*g*').

In the present paper, the result of temperature and intensity dependent photoconductivity follows second case as measurements have been taken in intermediate range. With the change in concentration of Zn, there occur some structural changes in the network due to the absence of long range order. Density of states and the distribution of localized states change. Effect of these modifications is to increase or decrease defect states in the alloy. Density of states is inversely proportional to the carrier lifetime means higher the density of states, lifetime will be lower. In the present case, the carrier lifetime (τ) decreases, which shows that density of defect states will increase. Defect states act as recombination centers in the presence of light. Table 2 presents that carrier lifetime decreases which lead to increase in density of states. This may be due to formation of intimate valence alternation pairs (IVAPS) under illumination. Defects are converted by bond switching reactions to random pairs of charged defects, known as light induced

Table 2 — Variation of γ, photosensitivity (σ_{ph}/σ_d), dispersion parameter (α), characteristic energy of density of states and characteristic temperature with the change in Zn concentration in the thin films of $Se_{90-x}Te_{10}Zn_x$ glassy alloys at the room temperature range (303 K)

Sample	γ	σ_{ph}/σ_d	τ_d (sec)	α	E_o(eV)	T_o(K)
$Se_{90}Te_{10}$	0.40	0.58	26	0.31	.087	1010
$Se_{88}Te_{10}Zn_2$	0.54	2.74	23	0.69	.038	440
$Se_{85}Te_{10}Zn_5$	0.54	0.86	21	0.80	.032	371
$Se_{80}Te_{10}Zn_{10}$	0.50	1.33	18	0.84	.031	360

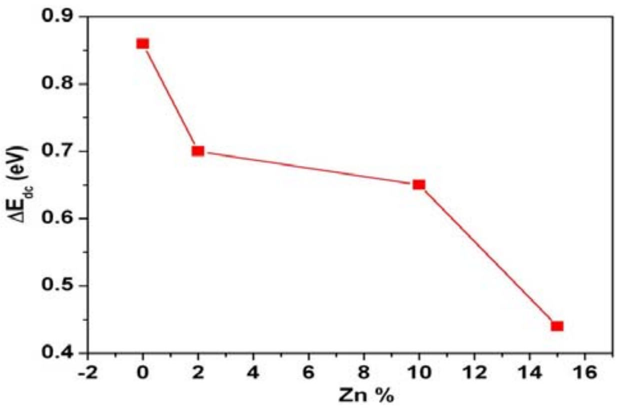

Fig. 3 — Variation of activation energy with Zn concentration in $Se_{90-x}Te_{10}Zn_x$ thin films

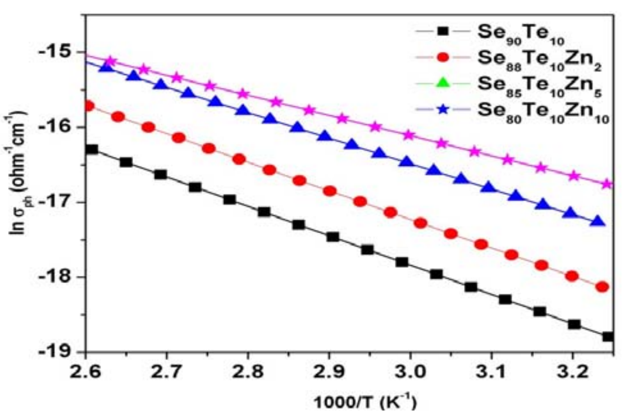

Fig. 4 — Temperature dependent photoconductivity in $Se_{90-x}Te_{10}Zn_x$ thin films

meta-stable defects[22-24] (LIMDS). LIMDS act as hole / electron trapping centers and decrease the photocurrent. Dependence of steady state photoconductivity on intensity (F) has been studied at room temperature (303K). Figure 5 shows the plots of lnσ_{ph} versus ln F. Plots show straight lines for all compositions, which show that photoconductivity (σ_{ph}) follows a power law with intensity, i.e.

$$\sigma_{ph} \propto F^{\gamma} \qquad \ldots (2)$$

For $\gamma = 1$, recombination is monomolecular in nature and for $\gamma = 0.5$, recombination is bimolecular. In the present case, photocurrent is found to be square-root-dependent on light intensity. For all $Se_{90-x}Te_{10}Zn_x$ compositions, value of γ lies between 0.40 and 0.54 which is near to 0.5 as given in Table 2. This confirms bimolecular recombination mechanism in the studied films. Value of γ between 0.5 and 1.0 shows the existence of continuous distribution of traps in the gap[25]. According to Simmons, value of γ between 0.5 and 1.0 can also be due to discrete energy levels in band gap. In amorphous semiconductors, photoconduction mechanism is based on recombination kinematics using the dangling bond levels. Atoms at the end of chain or open ring atomic units has an electron as a defect and this defect is neutral (D^o). Chalcogenides are negative correlation energy materials and defect sites with two electrons are favored. This means that negative charged (D^-) and positively charged (D^+) defects pin Fermi level near to the middle of band gap. D^- and D^+ defects act as acceptors or donors for trapping processes. In case of thermally activated processes on electron/hole transforms D^+/D^- in D^o (neutral dangling bond). Electron trapped in the level D^+ is transformed into D^o by :

$$D^+ + D^- \rightarrow D^o$$

This electron from D^o centre can combine with hole trapped on D^-level into D^o by:

$$D^- + h \rightarrow D^o$$

Number of photo carriers is equal to the excess of D^o centers, which appear by illumination. Under these conditions, value of γ is good with the supposition that recombination process takes place between an electron trapped on D^+ level and a hole trapped on D^- level, a bimolecular recombination. Photosensitivity is also calculated for $Se_{90-x}Te_{10}Zn_x$ thin films at an intensity of (3650 lux) and at room temperature (303 K), corresponding values are given in Table 2. Photosensitivity is maximum for $Se_{88}Te_{10}Zn_2$ after that it decreases at higher concentration of Zn. For understanding recombination and trapping mechanisms, and to determine the energy distribution of various species of gap states transient photoconductivity measurements have been taken by shining the light of intensity (3650 lux) at temperature (303 K) on sample. Rise and decay of photocurrent with time for all compositions are taken as shown in Fig. 6 which shows that photocurrent rises in a monotonic manner up to a steady state value. When light is switched off photocurrent starts to decay quite fast initially and reaches its steady state value or zero as time elapses as shown in Fig. 7. However, a persistent photoconductivity is not observed in composition of $Se_{90-x}Te_{10}Zn_x$. For single trap level, these curves must be straight lines. In the present case, curves are not straight means they do not have same slope and slope goes on decreasing as the decay time increases. This shows that traps exist at all energies in the band gap, having different time constants and give non-exponential decay of photoconductivity. For all analysis of decay rates in case of non-exponential decay, differential lifetime (τ) is calculated using the Fuhs and Stuke[26] relation.

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

For exponential decay, differential life time will be equal to the carrier life time. But, in case of non-exponential decay, differential lifetime (τ) increases with time and the differential life time at (t=0) gives the carrier lifetime value. From the slope of I_{ph} versus time the value of differential lifetime is calculated using Eq. (3) at different imes of decay curve.

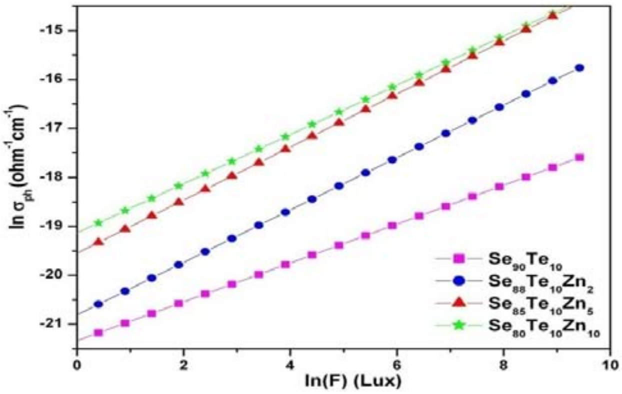

Fig. 5 — Intensity dependent photoconductivity in $Se_{90-x}Te_{10}Zn_x$ thin films

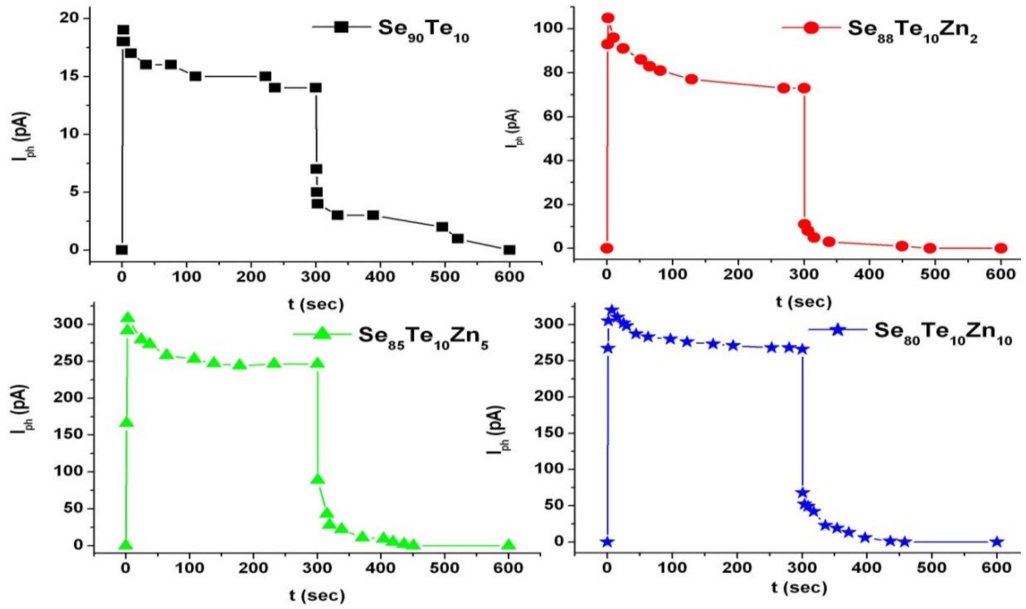

Fig. 6 — Rise and decay of photocurrent with time for $Se_{90-x}Te_{10}Zn_x$ thin films at 303 K

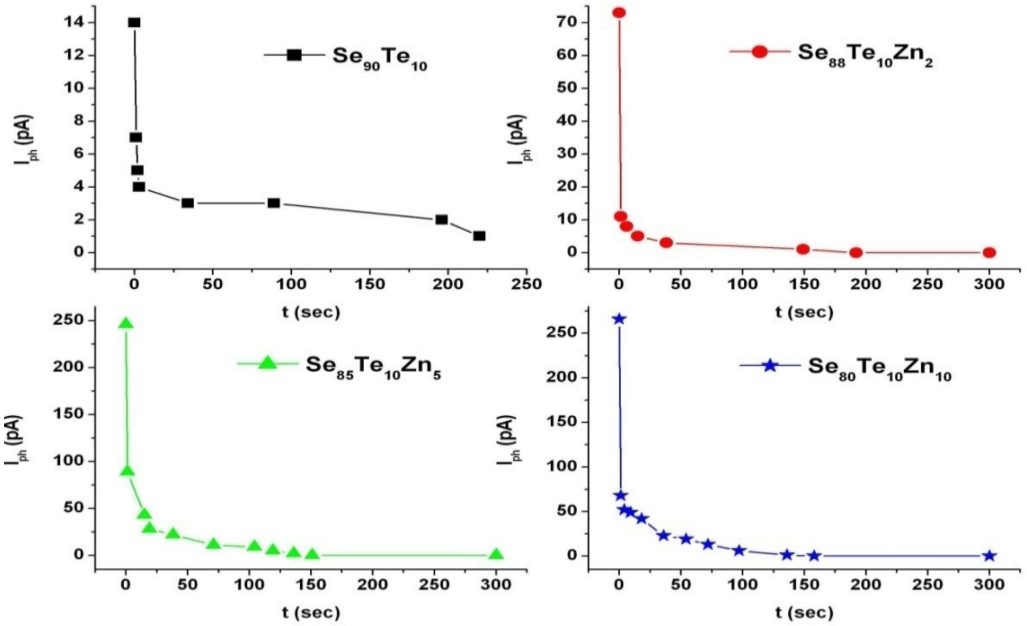

Fig. 7 — Decay of photocurrent with time for $Se_{90-x}Te_{10}Zn_x$ thin films at 303 K

Figure 8 shows the variation of differential lifetime (for $Se_{80}Te_{10}Zn_{10}$) with time at 303 K and at intensity (3650 lux). It is found that the value of differential lifetime increases with increase in time. This shows that the decay is non-exponential in nature. Other compositions show the same trend. Value of differential lifetime at (t=10 s) has been chosen to compare the rate of decay of all compositions. Differential lifetime decreases with increase in Zn concentration, lower value of differential lifetime after Zn addition shows slower rate of decay of photocurrent. Photocurrent rise and decay can be described by the trap-controlled recombination model of Iovu[27]. According to this model, photocurrent rise is fully controlled by carrier trapping yield $I_{ph} \sim G_o t^{\alpha}$. Here α is dispersion parameter and G_o is generation

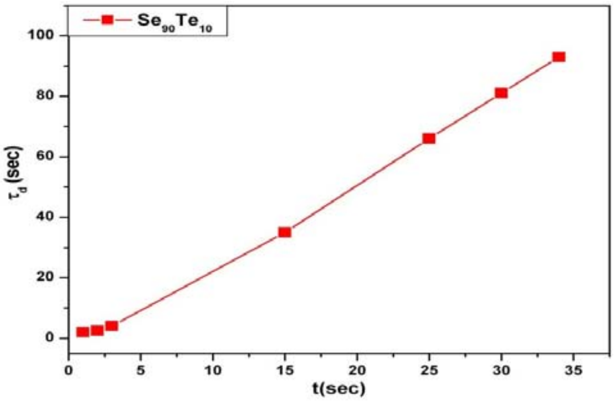

Fig. 8 — Behaviour of carrier lifetime (τ_d) with the increase in time for $Se_{90-x}Te_{10}Zn_x$ thin film at 303 K

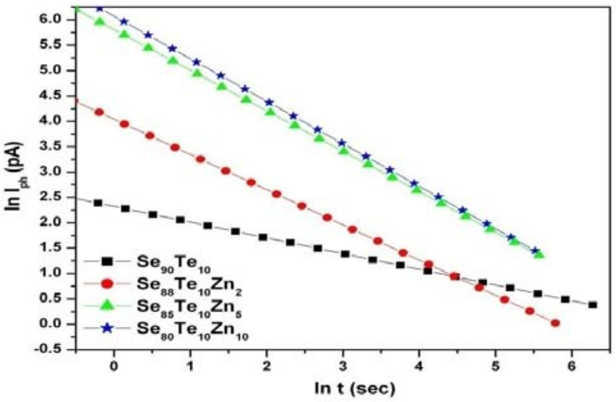

Fig. 9 — Variation of (ln I_{ph}) with (ln t) in $Se_{90-x}Te_{10}Zn_x$ thin films at 303 K

rate. After a long time, rise is due to excitation intensity. Decay of photocurrent depends on density of photo-generation pulse when total filling of gap states is not achieved then initial portion of decay governed by capture process exist and recombination is delayed. This portion I_{ph}~$I_o t^{-(1-\alpha)}$, here I_o is photocurrent at time when light is switched off. Further behaviour of transients depends on excitation intensity. At low generation intensity, starting portion turns to final decay, along which I_{ph}~$I_o t^{-(1+\alpha)}$. At higher generation intensity, an intermediate portion exists in the rise and decay curve where I_{ph}~$I_o t^{-1}$. Figure 9 shows the variation of ln (I_{ph}) with ln(t), using slope of this plot, value of the dispersion parameter (α) is calculated as given in Table 2. Using α, the localized state distribution parameter E_o is also calculated by the relation $\alpha = kT/E_o$, where k is Boltzmann constant and T is ambient temperature. E_o can also be calculated by using the relation $E_o=kT_o$, E_o is characteristic energy and T_o is characteristic temperature. According to Vaninov[28], T is the temperature at which impurities are frozen in chalcogenides during the cooling process. Value of dispersion parameter (α) decreases with increase in Zn concentration.

4 Conclusions

Dark *dc* conductivity and photoconductivity increase exponentially with increase in temperature, which shows that conduction is through thermally activated process and due to extended states. Activation energy decreases and conductivity increases with increase in Zn concentration that shows the density of states increase. Carrier lifetime decreases with the increase in Zn concentration that also confirms the density of states increase. Value of γ lies between 0.40 and 0.54 that shows the recombination is bimolecular in nature. Photosensitivity is maximum in $Se_{88}Te_{10}Zn_2$ thin films and then decreases with Zn concentration. Decay curves do not have the same slope and slope goes on decreasing as decay time increases. This shows that traps exist at all the energies in the band gap.

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