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TRANSIENT PHOTOCONDUCTIVITY IN a-$Se_{70}Te_{30-x}Zn_x$ THIN FILMS

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Rise and decay of photoconductivity is studied in amorphous thin films of a-$Se_{70}Te_{30-x}Zn_x$ (x = 0, 2, 4, 6 and 8) prepared by vacuum evaporation technique. These measurements at different temperatures and intensities indicate that the decay of photoconductivity is quite slow. A persistence photoconductivity is also observed. This is attributed to light induced effects in these materials. Photoconductivity decay, even after subtraction of persistent photoconductivity, is found to be non – exponential in the present case, indicating the presence of continuous distribution of defect states. Differential life time of execess carriers is calculated which supports the above argument.

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Keyword: Transient photoconductivity, differential life time, defect states, amorphous thin films.

1. Introduction

The changes in physical properties of amorphous films is caused by the modification of their structural and chemical disordering due to presence of high concentration of defects [1].

Transient photoconductivity measurements are, important for amorphous chalcogenide systems as the rise and decay is governed by the trpping effects due to the presence of inherent defect states in these materials. Such measurements have been made by various workers in past. It is generally reported that the decay of photoconductivity is quite slow in these materials.

The addition of third element also affect the decay process. The optical properties and photostructural changes of Ag-doped chalcogenide glasses have been studied by various workers [2-6]. Thin films of chalcogenide glasses containing Ag have found application in erasable phase change optical recording [7-12]. Different Ag doped chalcogenide alloys have been developed as recording layer and their good practical performance has been reported [7-12]. In case of Ag-doped glasses, much attention has been devoted to optical properties [2-6], but only a few studies have been performed on crystallization kinetics [13-15].

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 [16, 17]. The two serious problems are the limited reversibility [18], 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 [19-21].

The present paper reports measurements of the rise and decay of photoconductivity in a-$Se_{70}Te_{30-x}Zn_x$ thin films, where x = 0, 2, 4, 6 and 8 at. %. Differential life time of excess carrier trapped in defect level shows that density of defect centre are decreases. 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

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chalcogenide glasses [22-27]. There are successful reports of doping of Zn Se_x Te_{1-x} in the literature [28] that are suitable for the development of light emitting diodes and lasers.

2. Experimental

Glassy alloy of $Se_{70}Te_{30-x}Zn_x$ were 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} g. 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.

Thin films of glassy $Se_{70}Te_{30-x}Zn_x$ were 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 was ~ 500 nm .The coplanar structures are used for the present measurements.

For Photoconductivity 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 370 K for one hour in a vacuum of 10^{-2} torr.

3. Result and discussion

To measure the rise and decay of photoconductivity (σ_{ph}) with time, thin film samples were mounted in the metallic sample holder and light was shown through a transparent window. After light exposure, rise of conductivity was measured as the function of time. The initial dark value of conductivity was subtracted to obtain photoconductivity (σ_{ph}) during rise. The first set of measurements was taken at room temperature by varying the light intensity. A vacuum ~10^{-2} was maintained during the measurements. The experimental data for the rise of photoconductivity at different intensities for the case of a-$Se_{70}Te_{24}Zn_6$ in white light is plotted as a function of time in Fig.1. It is clear from this figure that photoconductivity rises monotonically with time and saturates after a long time (a few minutes). Initially, it increases rapidly and then become slower before reaching to steady state value. Similar results were observes for other samples.

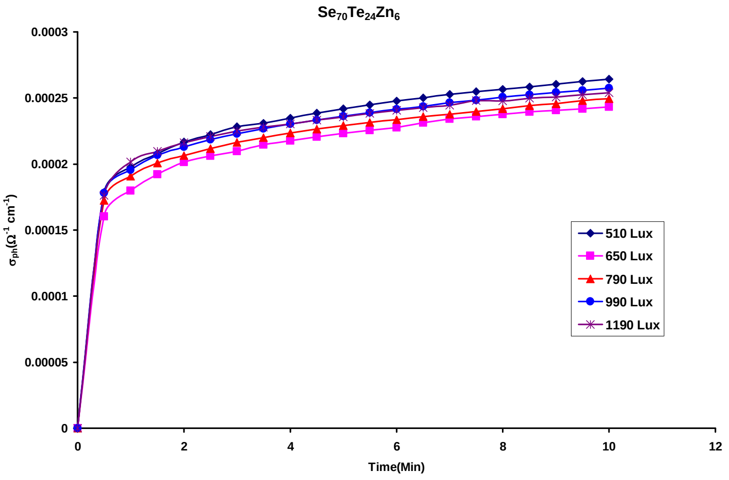

Fig. 1 Rise of photoconductivity with time at different intensities in $Se_{70}Te_{24}Zn_6$.

After attaining the steady state, light was turned off and the decay of photoconductivity was measured as the function of time. Fig.2 shows the results of these measurement in a-$Se_{70}Te_{24}Zn_6$ at different intensities. It is clear from this figure that the behaviour of the decay curves is of the same nature at different intensities. Initially, the photoconductivity decay is quite fast and then becomes slow as time elapse. A persistent photoconductivity is also observed which takes many hours to decay. The persistent photoconductivity is found to be more when the samples are exposed to higher intensities (see.Fig.2). Similar result were observes for other samples.

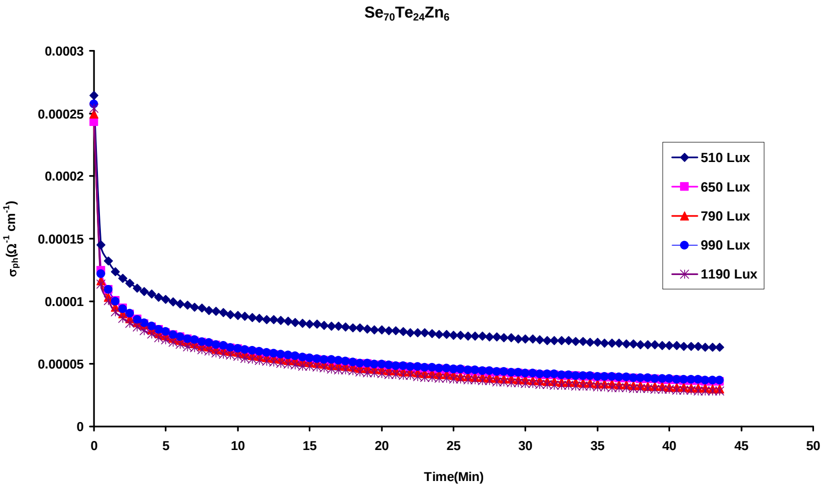

Fig. 2 Decay of photoconductivity with time at different intensities in $Se_{70}Te_{24}Zn_6$.

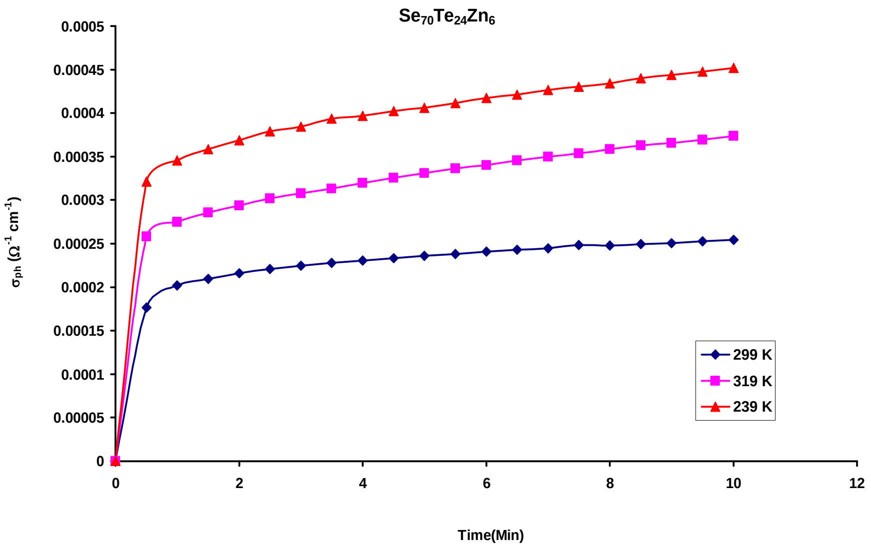

Fig. 3 Rise of photoconductivity with time at different temperature in $Se_{70}Te_{24}Zn_6$.

Another set of measurements was made at different temperatures keeping the intensity of light constant. The rise of photoconductivity in such a case in a-$Se_{70}Te_{24}Zn_6$ is shown in Fig.3. The behaviour of rise curves is similar. The corresponding decay of photoconductivity is shown in Fig.4. The behaviour of decay curves is also similar at different temperatures except that the persistent photoconductivity increases as temperature increases. Similar result were observes for other samples.

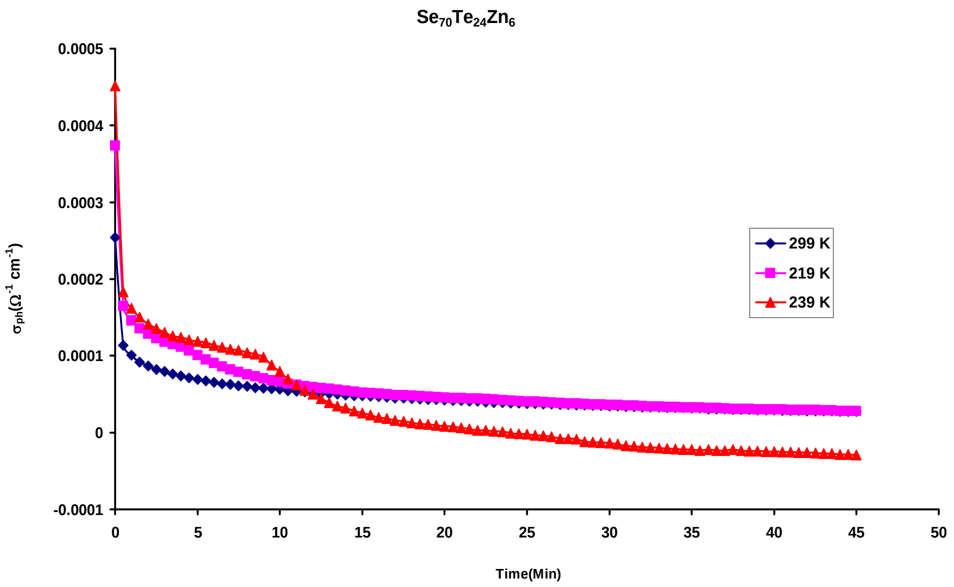

Fig. 4. Decay of photoconductivity with time at different temperature in $Se_{70}Te_{24}Zn_6$.

The persistent photoconductivity is observed in chalcogenide glasses by many workers [29-36] and is attributed to some kind of photo induced effects and not due to trapping of charge carriers in the traps [37] because of the large time constants involved.

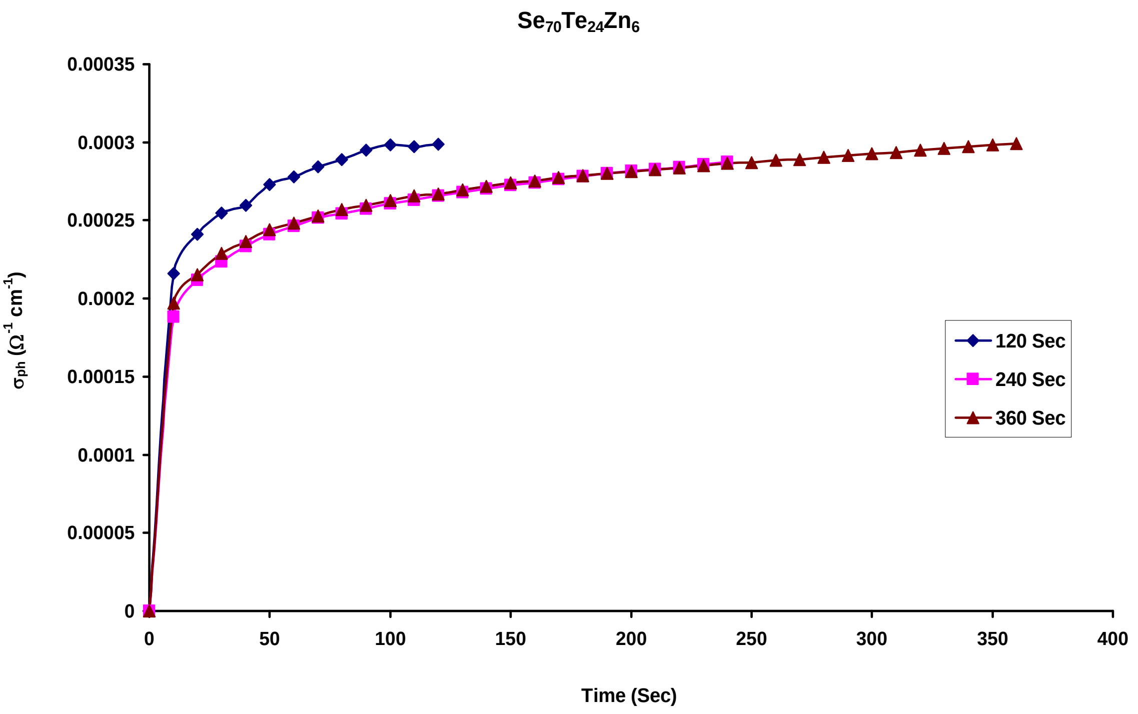

Fig. 5. Rise of photoconductivity with time at different temperature illumination of time in $Se_{70}Te_{24}Zn_6$.

Another set of measurements was made at different illumination of time keeping the intensity of light constant. The rise of photoconductivity in such a case in a-$Se_{70}Te_{24}Zn_6$ is shown in Fig.5. The behaviour of rise curves is similar. The corresponding decay of photoconductivity is shown in Fig.6. The behaviour of decay curves is also similar at different temperatures except that the persistent photoconductivity increases as temperature increases. Similar result were observes for other samples. Fig. 7 -9 shows decay of photoconductivity after subtraction of persistent of photoconductivity in thin films of a-$Se_{70}Te_{24}Zn_6$. Results are similar for all samples.

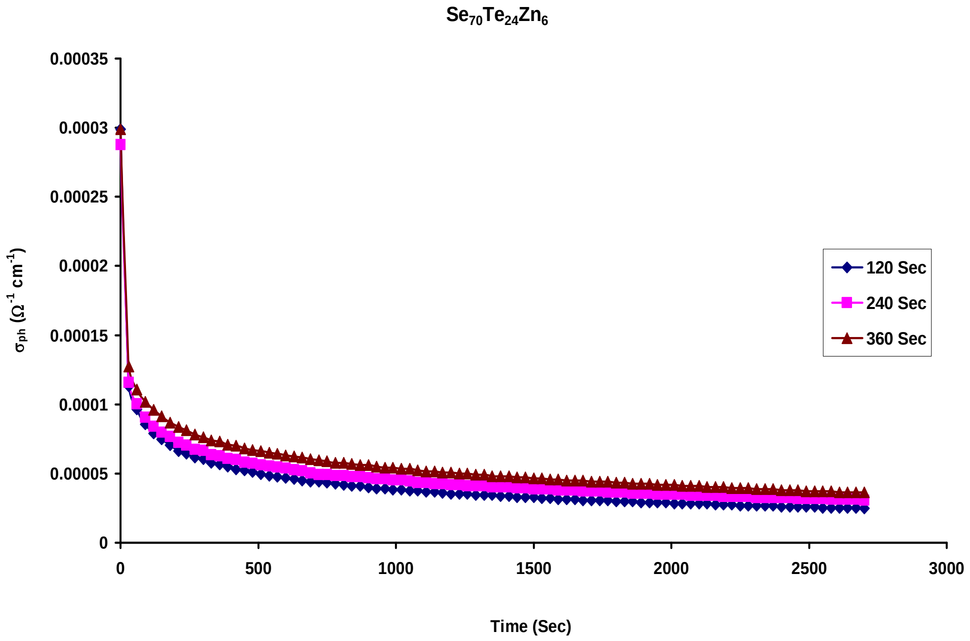

Fig. 6. Rise of photoconductivity with time at different illumination of time in $Se_{70}Te_{24}Zn_6$.

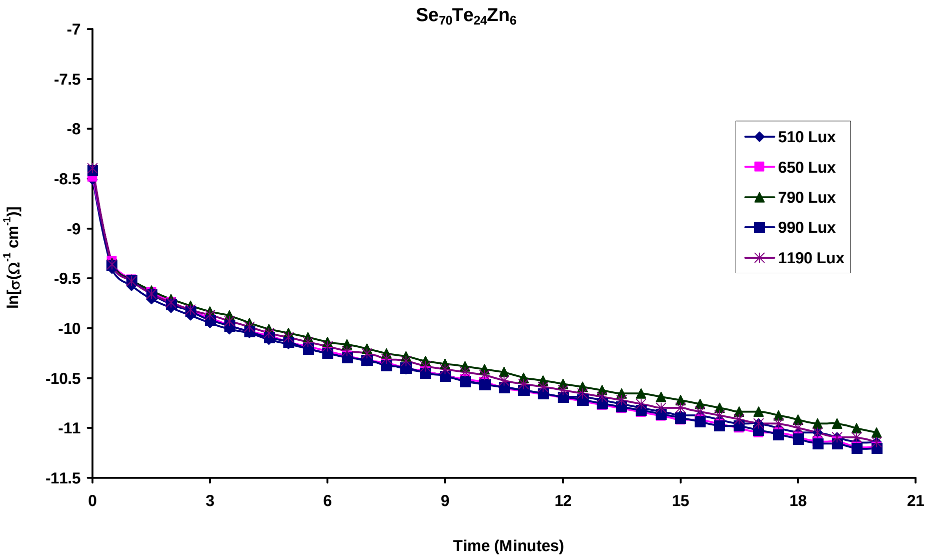

Fig. 7. Decay of photoconductivity with time at different intensities in $Se_{70}Te_{24}Zn_6$ after subtraction of photoconductivity.

To understand the trapping effects, the persistent photoconductivity is subtracted from the measured photoconductivity and then the natural log of corrected photoconductivity is plotted against time at different intensities in Fig.5, for a-$Se_{70}Te_{24}Zn_6$.

This curve must be straight line 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 exist at all the energies in the band gap, which have different time constants and hence give rise to the non – exponential decay of photoconductivity.

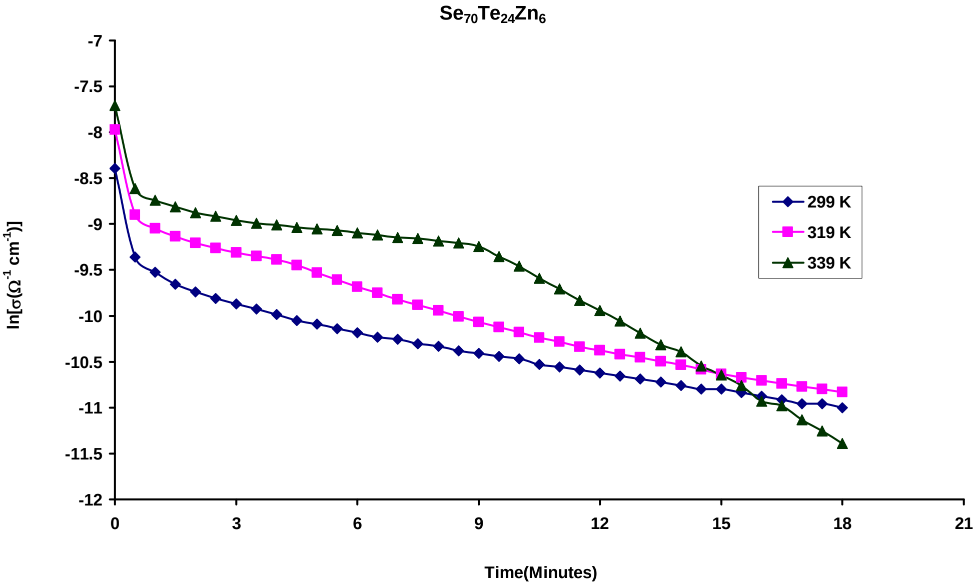

Fig. 8. Decay of photoconductivity with time at different temperature in $Se_{70}Te_{24}Zn_6$ after subtraction of photoconductivity.

To analyze the decay rates in case of non exponential decay, we prefer to use the concept of differential life time suggested by Fuhs and Stuke [38] which is given as

$$\tau_d = [1 / \sigma_{ph} (d\sigma_{ph} / dt]^{-1} \qquad (5)$$

In the case of exponential decay, the differential life time will be equal to the carrier life time. However, in the case of non- exponential decay τ_d will increase with time and only the value at t = 0 will correspond to carrier life time.

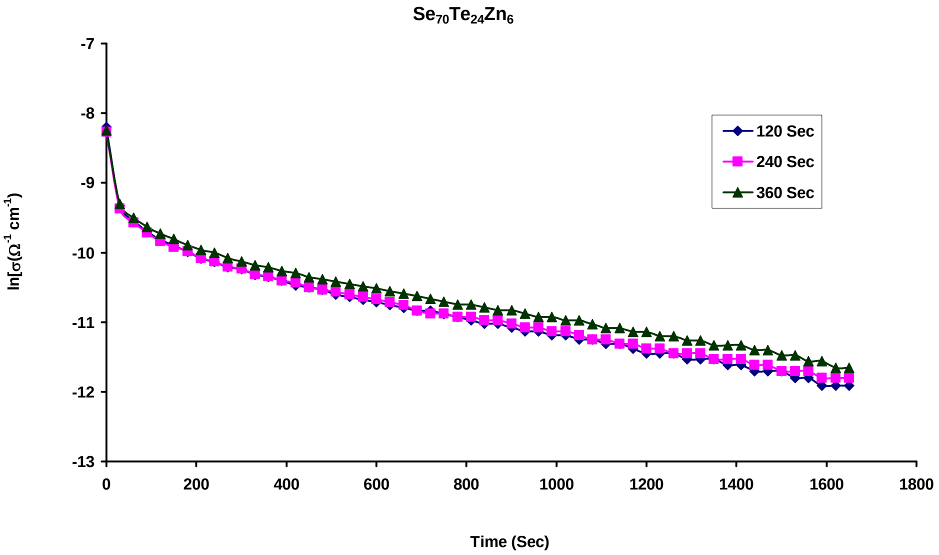

Fig. 9. Decay of photoconductivity with time at different illumination of time in $Se_{70}Te_{24}Zn_6$ after subtraction of photoconductivity.

From the slope of σ_{ph} vs time curves, we have calculated the values of τ_d using eq. (5) at various times of the decay curves of Fig.5. Similar results were obtained at other intensities also.

It is clear from Fig. 10, that τ_d increases with the increase in time in a-$Se_{70}Te_{24}Zn_6$. This confirms the non – exponentially decay in the present case as, for an exponential decay, $\tau_{d,}$ should be constant with time. Similar result were observes for other samples. From fig.11 it is cleared that density of defect states is maximum at percentage of 2 in composition of $Se_{70}Te_{30-x}Zn_x$.

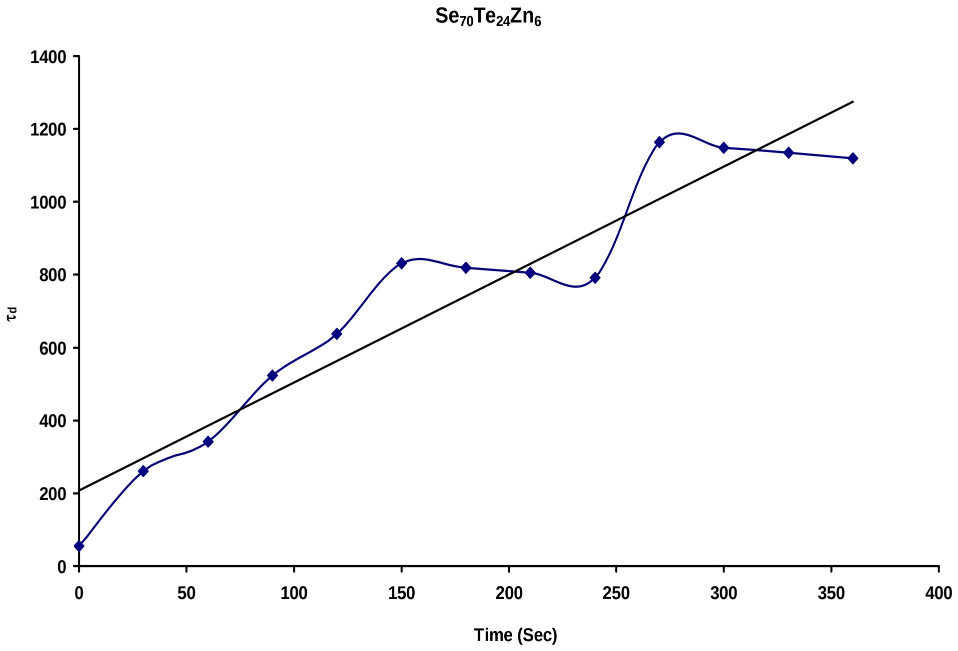

Fig. 10. Differential life time vs. time at temperature 299 K and intensity 1190 lux.

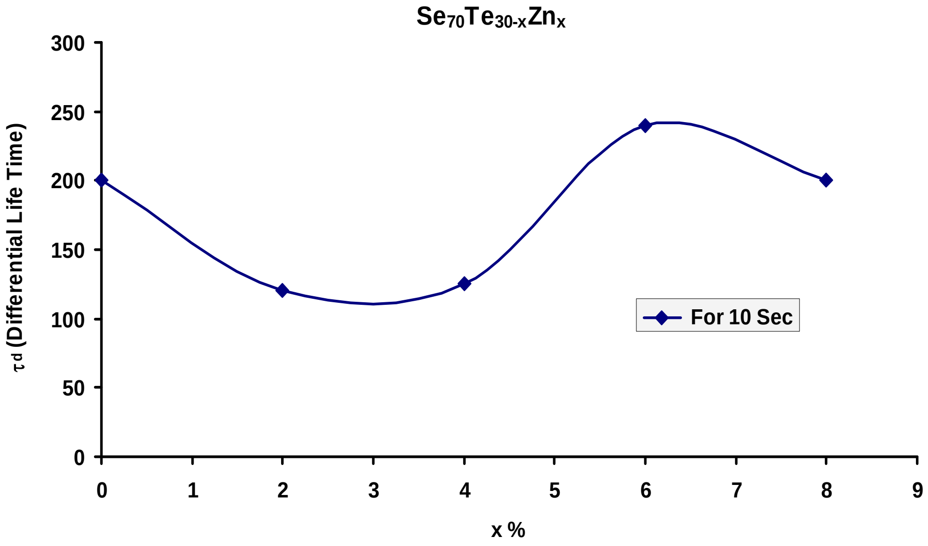

Fig.11. Variation of differential time with component of Zn(x %) for particular time difference of 10 seconds.

In chalcogenide glasses a discontinuity in various physical properties has been observed [39-46] at a particular composition when the average co-odination numbe <r> reaches 2.4. This is explained by Phillips and Thorpe [47] in terms of a mechanically optimised structure at a critical glass composition.

In the present case the co-ordination number of Se is 2, Te is 2 and that of Zn is 4. Hence, for a composition where the maximum in τ_d is occurring, <r> comes out to be 2.08 following the model of Phillips and Thorpe [47]. IV-VI glasses, however, show a threshold at <r> = 2.4 as pointed out by Phillips [48-50].

It may be mentioned here that Phillips considered the interaction between atoms to be purely covalent while arriving at the balance condition .Such an assumption may be valid for Ge-Se glasses but not for systems containing heavier elements such as Zn.The presence of heavier element may lead to partial covalent bonding .This can affect the balance condition .There are several other shortcomings in the simple theory, such as the assumption of the 8-N rule. It has been reported [51] that the co-ordination number of elements changes with composition and that the simple assumption of the co-ordination number of the elements on the basis of the 8-N rule in the balance condition is not strictly valid for such cases.

However, it should be noted that the the above explanation for this anomaly are highly qualitative and it is difficult to get any quantitative information from such explanations. Future experiments on the local structure of these glasses could reveal the exact origin and nature of the anomaly.

4. Conclusions

Transient photoconductivity measurements at different temperatures and intensities in a-$Se_{70}Te_{30-x}Zn_x$ (x = 0, 2, 4, 6 and 8) thin films indicate that the decay of photoconductivity has two components, initially; it is very fast and then become quite slow. This component is found to be non exponential in the present case indicating the presence of continuous distribution of defect states. A persistent photoconductivity is also observed, which increases at higher intensities. This is attributed to light induced effect in this material. Differential life time of excess carrier in defect energy state increases and density of localized defect states were decreases.

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