CHAPTER-SIX
CHAPTER – SIX
PHOTOCONDUCTIVITY OF Se-Ge-In
SYSTEM AT DIFFERENT TEMPERATURE

6.1 Introduction:

In the last few years, particular attention has been devoted to the study of the physical properties of chalcogenide glasses in view of its possible application in photovoltaic devices. Therefore much work has been done on both bulk and thin film samples of glassy chalcogenide regarding electrical and optical properties [79-81]. The common feature of these glasses is the presence of localized states in the mobility gap as a result of the absence of long-range order as well as various inherent defects. The investigation of electron transport in disordered systems has gradually been developed and the investigation of gap states is of particular interest because of their effect on the electrical properties of semiconductors [156, 157].

On the other hand, Barisova [158] suggested as Cu or Ge content increased in Cu-Ge-Te glasses, a progressive replacement of weak van der Waals bonds which strengthening the glass structure. Ramesh el. al. [159] studied the crystallization process of Cu\textsubscript{x} Ge\textsubscript{15} Te\textsubscript{85-x} glasses. These glasses exhibit a single crystallization stage. Vazquez el. al. [160] reported the glass formation and diversification of alloys in the Cu-Ge-Te system by differential scanning
calorimetry. They presented a comparison of various simple quantitative methods to assess the level of stability of the glassy materials in the above mentioned system. All of these methods are based on characteristic temperatures such as the glass transition temperature $T_g$, the onset temperature of crystallization $T_{in}$, the temperature corresponding to the maximum crystallization rate, $T_p$ or melting temperature $T_m$. Electrical resistivity measurements under pressures at ambient and low temperatures have been carried out on bulk, melt quenched $Cu_xGe_{15}Te_{85-x}$ glasses ($2 < x < 10$) by Ramesh el. al. [161]. They found that the resistivities of these samples decrease continuously with pressure. Electrical and optical properties of $Ge_xSe_{1-x}$ thin films have been studied most extensively [162-164]. When tellurium atoms are used instead of selenium, most of the observations are not valid. Thus it appears that Te atoms exhibit typical properties. From the above it is clear that very little attention is paid to photoconductive properties of Se-Ge-In system.

In this chapter we deal with new results associated with the photoconductive properties of $Se_{80}Ge_{20-x}In_x$ where $x = 0, 2, 4, 6, 8, 10 & 20$ combinations of thin films at different temperatures. The present work is mainly concerned with some experimental observations on the effect of temperature on the photoconductive properties of the above combination thin films.
6.2 Result and Discussion:

Photoconductivity measurements can be made with the thin film samples which were mounted in a specially designed sample holder. The sample holder has a transparent window to shine light for these measurements in a vacuum \( \sim 10^{-2} \) Torr. The temperature of the films was controlled by mounting a heater inside the sample holder and measured by a calibrated copper–constantan thermocouple mounted very near to the films.

A 200W tungsten lamp was used as a source of light and the intensity of light was varied by changing the voltage across the lamp. The intensity measurements were made by a lux-meter.

A 10V d.c. voltage was applied across the film and the resulting current was measured by a digital Electrometer (Keithley, model 614). The heating rate was kept quite small (0.5 K/min) for these measurements.

The photoconductivity was calculated by measuring current increase due to light shining. For this purpose, the current was measured in presence of light \( (I_L) \) as well in dark \( (I_0) \). The subtraction of these two values gave the value of photocurrent \( (I_{ph}) \).

Before measuring the dark and photoconductivity, the films were first annealed at 375K for 1 h in a vacuum \( \sim 10^{-2} \) Torr. I–V characteristics are found linear and symmetric up to 30V in all glasses studied. The present measurements are, however, made by applying only 10V across the films.
The steady-state and transient photoconductivity measurements in amorphous thin films of Se$_{80}$Ge$_{20-x}$In$_x$ ($x = 0, 2, 4, 6, 8, 10$ and $20$) prepared by vacuum evaporation technique are reported in this chapter. Temperature dependence of steady state photoconductivity is studied at different light intensities. Decay of photoconductivity is studied at different temperatures (i.e. at 310, 350 and 375K) and intensities.

Glassy alloys of Se$_{80}$Ge$_{20-x}$In$_x$ ($x = 0, 2, 4, 6, 8, 10$ and $20$) were prepared from the melt by the quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed using an electronic balance with the least count of $10^{-4}$ gm. The materials were then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampoules of about 8 mm diameter. The ampoules containing Se$_{80}$Ge$_{20-x}$In$_x$ ($x = 0, 2, 4, 6, 8, 10$ and $20$) were heated to $1000^\circ C$ and were held at that temperature for 12 h. The temperature of the furnace was raised slowly at a rate of $3-4^\circ C/min$.

During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogenous glassy alloys. The melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water. The quenched samples were then taken out by breaking the quartz ampoules.

Thin films of these glasses were prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated
indium electrodes at bottom were used for the electrical contact. The thickness of the films was ~500 nm. The co-planar structure (length ~1.2 cm and electrode separation ~0.5 mm) was used for the present measurements.

For the measurements of photoconductivity, thin film samples were mounted in a specially designed sample holder which has a transparent window to shine light for these measurements in a vacuum ~10^{-2} Torr. The temperature of the films was controlled by mounting a heater inside the sample holder and measured by a calibrated copper-constantan thermocouple mounted very near to the films.

The source of light was a 200W tungsten lamp. The intensity of light was varied by changing the voltage across the lamp. The intensity was measured by a lux-meter.

A d.c. voltage of 10V is applied across the film and the resulting current is measured by a digital Electrometer (Keithley, model 614). The heating rate is kept quite small (0.5 K/min) for these measurements.

The photoconductivity is calculated by measuring current increase due to light shining. For this purpose, the current was measured in presence of light ($I_L$) as well in dark ($I_d$). The subtraction of these two values gave the value of photocurrent ($I_{ph}$).

Before measuring the dark and photoconductivity, the films were first annealed at 370K for 1 h in a vacuum ~10^{-2} Torr. I–V characteristics are
found linear and symmetric up to 30V in all glasses studied. The present measurements are, however, made by applying only 10V across the films.

Now the set of measurements was taken at different temperatures i.e. 310, 350 and 375K by varying the light intensity keeping the illumination time constant (30 min in the present case). A vacuum $\sim 10^{-2}$ was maintained during the measurements. The experimental data for the decay at different intensities for the case of Se$_{80}$Ge$_{20-x}$In$_x$ ($x = 0, 2, 4, 6, 8, 10$ and $20$) in white light is plotted as a function of time in Fig. 6.1 to Fig. 6.7. The results for all the glasses were of the same nature but the initial value of the $\sigma_{ph}$ increases slightly as the indium percentage increases from 0 to 20.

It is clear from these figures that the behavior of the decay curves is of the same nature at different temperatures. Initially, the photoconductivity decay is quite fast and then becomes slow as time elapses. 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. 6.1 to Fig 6.7).

The behavior of the decay curves is similar at different temperatures except that the persistent photoconductivity increases as temperature of measurement increases. The persistent photoconductivity is observed in chalcogenide glasses by many workers [148-152] and is attributed to some kind of
Figure 6.1 Time dependence of Photoconductivity at different temperatures during decay in $\alpha$-Se$_{80}$Ge$_{20}$ thin films.
Figure 6.2 Time dependence of Photoconductivity at different temperatures during decay in a-Se_{80}Ge_{18}In_{2} thin films.
Figure 6.3 Time dependence of Photoconductivity at different temperatures during decay in a-Se$_{80}$Ge$_{16}$In$_4$ thin films.
Figure 6.4 Time dependence of Photoconductivity at different temperatures during decay in a-Se$_{80}$Ge$_{14}$In$_6$ thin films.
Figure 6.5 Time dependence of Photoconductivity at different temperatures during decay in a-Se$_{80}$Ge$_{12}$In$_8$ thin films.
Figure 6.6 Time dependence of Photoconductivity at different temperatures during decay in a-Se$_{80}$Ge$_{10}$In$_{10}$ thin films.
Figure 6.7 Time dependence of Photoconductivity at different temperatures during decay in a-Se$_{80}$In$_{20}$ thin films.
photo-induced effects and not due to trapping of charge carriers in the traps [153] because of the large time constant involved.

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 temperatures in Fig. 6.8 to Fig. 6.14, respectively. The results of all the samples were of the same nature except the magnitude which increases slightly with the variation of the indium percentage. 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 exist at all the energies in the band gap which have different time constant and hence giving the non-exponential decay 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 [154] which is given as

\[ \tau_d = \left[ \frac{1}{\sigma_{\text{ph}} (d\sigma_{\text{ph}}/dt)} \right]^{-1} \]  

(6.1)

In the case of exponential decay, the differential lifetime will be equal to the carrier life time. However, in case of a non-exponential decay \( \tau_d \) will increase with time and only the value at \( t = 0 \) will correspond to the carrier lifetime.
Figure 6.8 Time dependence of Photoconductivity at different temperatures during decay in a-Se$_{80}$Ge$_{20}$ thin films after subtraction of persistent photoconductivity.
Figure 6.9 Time dependence of Photoconductivity at different temperatures during decay in a-Se$_{80}$Ge$_{18}$In$_2$ thin films after subtraction of persistent photoconductivity.
Figure 6.10 Time dependence of Photoconductivity at different temperatures during decay in a-\text{Se}_{80}\text{Ge}_{16}\text{In}_{4} thin films after subtraction of persistent photoconductivity.
Figure 6.11 Time dependence of Photoconductivity at different temperatures during decay in a-Se$_{80}$Ge$_{14}$In$_{6}$ thin films after subtraction of persistent photoconductivity.
Figure 6.12 Time dependence of Photoconductivity at different temperatures during decay in a-Se_{80}Ge_{12}In_{8} thin films after subtraction of persistent photoconductivity.
Figure 6.13 Time dependence of Photoconductivity at different temperatures during decay in a-Se$_{80}$Ge$_{10}$In$_{10}$ thin films after subtraction of persistent photoconductivity.
Figure 6.14 Time dependence of Photoconductivity at different temperatures during decay in a-Se$_{80}$In$_{20}$ thin films after subtraction of persistent photoconductivity.
Figure 6.15 Time dependence of differential life time at different temperatures during decay in a-Se$_{80}$Ge$_{20}$ thin films.
Figure 6.16 Time dependence of differential life time at different temperatures during decay in a-Se\textsubscript{80}Ge\textsubscript{18}In\textsubscript{2} thin films.
Figure 6.17 Time dependence of differential life time at different temperatures during decay in a-Se_{80}Ge_{16}In_{4} thin films.
Figure 6.18 Time dependence of differential life time at different temperatures during decay in a-Se$_{80}$Ge$_{14}$In$_6$ thin films.
Figure 6.19 Time dependence of differential life time at different temperatures during decay in a-Se$_{80}$Ge$_{12}$In$_8$ thin films.
Figure 6.20 Time dependence of differential life time at different temperatures during decay in $a\text{-Se}_{80}\text{Ge}_{10}\text{In}_{10}$ thin films.
Figure 6.21 Time dependence of differential life time at different temperatures during decay in a-Se$_{80}$In$_{20}$ thin films.
From the slope of $\sigma_{\text{ph}}$ vs. time curves, we have calculated the values of $\tau_d$ using Eq. (6.2) at various times of the decay curves of Figs. 6.8 to 6.14. The results have been plotted in Figs. 6.15 to Fig 6.21 in case of a $\text{Se}_{80}\text{Ge}_{20-x}\text{In}_x$ ($x = 0, 2, 4, 6, 8, 10$ and $20$). The results for other samples were of the same nature. It is clear from these figures that $\tau_d$ increases with the increase of time. This confirms the non-exponential decay in the present case as, for an exponential decay $\tau_d$ should be constant with time. A decrease of $\tau_d$ with increasing temperature is consistent with the decay of photoconductivity in presence of traps [155].

Temperature dependence of dark and steady state photoconductivity is studied in amorphous thin films of $\text{Se}_{80}\text{Ge}_{20-x}\text{In}_x$ ($x = 0, 2, 4, 6, 8, 10$ and $20$), prepared by vacuum evaporation technique, in the temperature range 293–373 K.

Temperature dependence of photoconductivity measurements at different intensities indicate that photoconductivity is also thermally activated in the above temperature range in all the samples studied as in case of dark conductivity. The activation energy of photoconduction is found to decrease with the increase in the intensity which indicates the shift of the Fermi level on light shining due to splitting of Fermi level into quasi-Fermi levels.

Transient photoconductivity measurements at different temperatures indicate that 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 photocurrent is also observed which increases at higher temperatures. This is attributed to light-induced effects in these materials.