CHAPTER 6

Photo-Electrical Properties of Se-Te-Cd & Se-Te-Ag Glassy Alloys
Chapter-6

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6.1 Introduction:

In recent times, great attention has been given to chalcogenide glasses mainly due to their wide range of applications in solid state devices both in scientific and technological fields. There has been an increased interest in the properties of Se-rich chalcogenide glassy alloys due to their current use as photoreceptors in TV vidicon pickup tubes [1] and in digital X-ray imaging [2]. The inadequacy of pure Se for its practical application includes its short lifetime, low sensitivity and low thermal instability. It has been pointed out that Se-Te alloys have more advantages than pure Se from the technological point of view due to their greater hardness, higher crystallization temperatures, higher photosensitivity and smaller aging effect [3-4]. Therefore, binary Se-Te alloys are used to extend the utility of a-Se.

Ag-doped chalcogenide glasses have become attractive materials for fundamental research of their structure, properties and preparation [5-9]. They have many current and potential applications in optics and optoelectronics such as photo doping, optical imaging, photo lithography and phase change (PC) optical recording [10-16]. Therefore the effect of incorporation of Ag in binary a-Se-Te is interesting to observe.

As ionic in nature, Ag doped chalcogenide glasses exhibit interesting electrical and optical properties, characteristic of ionic conductors and semiconductors. That is, the electrical conductivity is governed by Ag+ ionic conduction since the hole conductivity is substantially smaller and electron conductivity is not detected [17-18]. Since the photoconductivity kinetics of amorphous semiconductors are to a great extent determined by the process of trapping of non-equilibrium charge carriers on localized centers of various depths, such studies are important to understand the energy distribution of the traps. From application point of view also photoconductive properties are important.

The semi-conducting compounds belonging to the cadmium chalcogenide family such as CdSe_{x}Te_{1-x} can be advantageously used for various technical applications in particular for the conversion in photovoltaic or photo-electrochemical devices. This material with its near-ideal
band gap and a high optical absorbance is a promising material for low-cost terrestrial applications [19-22]. Attempts have been made to produce stable glasses which have good photosensitive properties and can be doped n or p type. The effect of incorporation of third element in binary chalcogenide glassy alloys has always been an interesting problem in getting relatively stable glassy alloys as well as to change the conduction from p to n as most of these glasses show p type conduction only.

Though the electrical and optical properties of these glasses have been studied by various workers the photoconducting properties of these glasses have not been studied in detail. Since the photoconductivity kinetics of amorphous semiconductors are to a great extent determined by the process of trapping of non-equilibrium charge carriers on localized centers of various depths, such studies are therefore important to understand the energy distribution of the traps. From application point of view also photoconductive properties are important. The photoconductivity has been measured as a function of temperature, intensity and wavelength of light by various workers in chalcogenide glasses and many models have been suggested for the recombination mechanism. The treatment differs in the model used for the density of gap states and the transition involved. In general, two different approaches have been adopted. The first one considers a slowly varying trap distribution consistent with the Cohen – Fritzche - Ovhinsky model of the band structure. Several variants of the original model have been introduced to interpret the photoconductivity data in chalcogenide glasses [23].

The present chapter reports the steady state and transient photoconductivity measurements in amorphous thin films of Se\(_{80-x}\)Te\(_{20}\)Cd\(_x\) (x =0, 5, 10 and 15) and Se\(_{80-x}\)Te\(_{20}\)Ag\(_x\) (where x = 0 and 4) glassy system prepared by vacuum evaporation technique. Temperature dependence of steady state photoconductivity is studied at different light intensities. Intensity dependence of photoconductivity is studied at different fixed temperatures. Composition dependence of various photoconductive parameters is also discussed. Section 6.2 describes the theory of Photoconductivity. The details of measurements and results and discussions have been presented in sections 6.3 and 6.4. The conclusions have been presented in the last section.

### 6.2 Theory of Photoconductivity:

#### 6.2.1 A Non-equilibrium Conductivity:

The process of formation of free charge carriers requires energy for overcoming the energy gaps between allowed bands or between local impurity levels and these bands. Under normal conditions this energy is drawn from reservoir of thermal energy present in the matter and under
such conditions the lattice and electrons temperatures are practically identical. Heating a semiconductor amplifies the intensity of the thermal vibrations of atoms (or ions) at lattice sites and simultaneously changes the electron energy distribution. At the same time the number of electrons in the conduction band and holes in the valence band are altered.

Free electrons and holes having densities corresponding to thermal equilibrium (i.e. equilibrium between the electrons and the lattice) are termed as “equilibrium carriers”. In the dark, under the condition of thermal equilibrium, the thermally generated carriers are distributed among the available energy states according to Fermi statistics. These electrons and holes occupying conduction states determine the dark electrical conductivity of the material, which can be expressed as

\[ \sigma = n_0 e \mu_n + p_0 e \mu_p \]  

(6.1)

where \( n_0 \) and \( p_0 \) are the densities of free electrons and holes respectively and \( \mu_n \) and \( \mu_p \) are the electron and hole mobility.

When a semiconductor under thermal equilibrium is exposed to light, excess charge carriers are generated by absorption of energy of light quanta. In contrast to thermal energy, the energy used to generate excess carriers is retained mainly by the electrons and the average thermal energy of the specimen lattice remains practically unaffected. Consequently, the thermal equilibrium between the lattice and electron is disturbed. Therefore, carriers formed in some way other than by thermal ionization are called “non-equilibrium carriers”. Obviously when photo excitation ceases to act, the thermal equilibrium between the lattice and electron will be re-established. The process of re-establishing equilibrium between the lattice and electrons reduces to the recombination of non-equilibrium carriers. The temperature of the lattice and the specimen remains practically unchanged.

Taking this into account it may be assumed that the application or removal of an excitation (i.e. illumination of semi-conducting material) changes the density of non-equilibrium carriers without affecting the density of equilibrium ones, and therefore, the total density \( (n \) or \( p) \) is simply the sum of the equilibrium and non-equilibrium carrier densities:

\[ n = n_0 + \Delta n \]  

(6.2)

\[ p = p_0 + \Delta p \]  

(6.3)

where \( \Delta n \) and \( \Delta p \) represents non-equilibrium electrons and holes densities respectively.

The presence of non-equilibrium carriers alters the conductivity of a semiconductor and in general case this can be written as:
Subtracting equation (4.1) from equation (4.4) one can get the non-equilibrium conductivity or photoconductivity as:

\[
\Delta \sigma = e (\mu_n \Delta n + \mu_p \Delta p)
\]

Thus, Photoconductivity may be defined as the enhancement of electrical conductivity of matter produced by the motion of carriers created by absorbed radiation. When a semiconductor is illuminated with lights of wavelengths lying in the fundamental absorption region, the absorption of light quanta produces electron transitions from the valence band to the conduction band and consequently generates non-equilibrium electrons and holes.

Let \( F \) be the intensity of light, then the amount of light energy absorbed per unit time in unit area of a layer of thickness \( dx \) is proportional to \( F \) and the layer thickness \( dx \):

\[
-dF = kF \, dx
\]

where \( k \) is a coefficient of proportionality, known as optical absorption coefficient.

The optical energy absorbed per unit time in unit volume is:

\[
\frac{dF}{dx} = kF
\]

If \( \Delta n' \) and \( \Delta p' \) represent the number of electrons and holes generated per unit time in a unit volume respectively, then

\[
\Delta n' = \Delta p' = \beta kF
\]

where \( \beta \) is a coefficient of proportionality.

If \( F \) represents the number of quanta per unit time, then \( \beta \) represents "quantum yield" i.e. the number of pairs formed by a single quantum.

Let us assume that illumination began at a certain moment and no other processes took place except carrier liberation. In such case, the number of non-equilibrium carriers would increase with time without limit according to the law:

\[
\Delta n = \Delta p = \beta kFt
\]

But this is not the actual case. Experimental data shows that in fact, after the certain time from the commencement of illumination a constant (steady-state) photoconductivity \( \Delta \sigma_{st} \) is established corresponding to steady state values of the non-equilibrium carrier densities \( \Delta n_{st} \) and \( \Delta p_{st} \).

It follows, therefore, that along with the process of generation of free carriers there must be a converse process of carrier annihilation and the rates of both processes must be equal when steady state is reached. This converse process is the recombination of non-equilibrium electrons.
and holes. Obviously the rate of recombination is directly related to the non-equilibrium carrier densities, since at the commencement of illumination when there are still few non-equilibrium carriers this rate is low. But later, as the number of such carriers increases, the rate of recombination increases becoming equal to the rate of generation. This corresponds to the steady-state non-equilibrium conductivity.

To express the value of steady state density in terms of parameters representing the process of the interaction of light with matter, the concept of lifetime of non-equilibrium carriers is introduced. Each non-equilibrium carrier liberated by light exists in the Free State for a certain time while it recombines (this is so called Free State lifetime). This lifetime may of course be different for different carriers. For this reason an average carrier lifetime is introduced with the notation $\tau_n$ for electrons and $\tau_p$ for holes.

Thus the steady state electron density $\Delta n_{st}$ may be written in the form of the product of the number of carriers liberated by light per unit time in unit volume ($\Delta n' = \beta k F$) and the average lifetime of their existence in the band before recombination $\tau_n$:

$$\Delta n_{st} = \beta k F \tau_n \quad \text{(6.10)}$$

Similarly for holes

$$\Delta p_{st} = \beta k F \tau_p \quad \text{(6.11)}$$

Therefore, one can write

$$\Delta \sigma_{st} = \Delta \sigma_n + \Delta \sigma_p \quad \text{(6.12)}$$

or,

$$\Delta \sigma_{st} = e \beta k F \left( \mu_n \tau_n + \mu_p \tau_p \right) \quad \text{(6.13)}$$

In the case of unipolar non-equilibrium conductivity due to carrier of one sign only

$$\Delta \sigma_{st} = e \mu \tau \beta k F \quad \text{(6.14)}$$

In this way the steady state non-equilibrium conductivity is governed by four parameters: $\mu, \tau, \beta \& k$. Two of these ($\beta \& k$) represent the interaction of light with matter and govern the process of generation of non-equilibrium carriers, while the other two ($\mu \& \tau$) describe the process of motion and recombination of non-equilibrium carriers.

### 6.2.2 Steady State Photoconductivity and the Lux-Ampere Characteristic:

The instantaneous lifetime $\tau$ for the rise curves may be given as:
In the non-linear case, a relaxation process has an infinite number of values of \( \tau \). However, one of these values has a special meaning: this is the lifetime under steady state conditions \( \tau_{st} \). In the steady state case, \( \frac{d (\Delta n)}{dt} = 0 \), so the equation (6.15) reduces to

\[
\tau_{st} = \frac{\Delta n}{\beta kF} \quad \text{(6.17)}
\]

This is why \( \tau_{st} \) is used as an important characteristic of recombination process. Obviously, in the linear case we have

\[
\tau = \text{const.} \quad \text{(6.18)}
\]

In general, the steady state density is given by

\[
\Delta n_{st} = \tau_{st} \beta kF \quad \text{(6.19)}
\]

In the linear case \( \tau_{st} \) is a constant, independent of the intensity of illumination, and consequently the steady state non-equilibrium density is proportional to the illumination intensity, i.e.

\[
\Delta n_{st} \propto F \quad \text{(6.20)}
\]

In any non-linear recombination case \( \tau_{st} \) depends on the illumination intensity and therefore there is no longer a linear relationship between \( \Delta n_{st} \) and \( \tau \). In particular, in the quadratic recombination case, \( \tau_{st} = \frac{1}{\sqrt{\beta kF}} \), and consequently

\[
\Delta n_{st} \propto \sqrt{F} \quad \text{(6.21)}
\]

Thus, the linear recombination case is characterized by a linear dependence on the intensity of illumination and the non-linear recombination case by a non-linear characteristic.

It should be noted here that all the recombination described above are valid only in the absence of trapping centers. The variation of \( \Delta n_{st} \) as \( F^{1/2} \) expected for trap free material is changed to a linear variation of \( \Delta n_{st} \) with \( F \) for a material with a uniform distribution of traps. A variation of \( \Delta n_{st} \) as \( F^{1/2} \) can be found even with trapping. However, if the density of photoexcited electrons trapped above the electron Fermi level is greater than the density of photoexcited electrons trapped...
below the Fermi level. The experimental observation of a variation of $\Delta n_d$ with a power of $F$ between 0.5 and 1.0 can be described by assuming an exponential distribution of traps.

The first model of photoconductivity in amorphous chalcogenides at higher temperature was proposed by Street and Mott [24]. In this model recombination of photo-generated carriers is dominated by deep centers situated close to the Fermi level [25]. According to this model $\sigma_{ph}$ must be proportional to product of the quantum efficiency $\eta$ and the light intensity $F$, when the photocurrent $I_{ph}$ is less than the dark current $I_d$, whereas at larger values of $F$, which yields $I_{ph} > I_d$, $\sigma_{ph}$ must be proportional to $(\eta F)^{1/2}$. This model describes well the experimental data on these materials.

A maximum in the photoconductivity is a general feature of amorphous semiconductors [26-29] and various theories have been put forward to explain this maximum. According to ABFH (Arnoldussen-Bube-Fegen-Holemberg) model [26] for photoconductivity in amorphous chalcogenide alloys, this type of behaviour is found in type I photoconductors. For type I photoconductors, photoconductivity is greater than the dark conductivity up to a particular temperature $T_{max}$ where the photoconductivity attains its maxima value. If the temperature is increased beyond $T_{max}$, photoconductivity decreases. On the basis of the energy level diagram suggested by the ABFH model, there are transitions which are from (i) localized to extended state for $T > T_{max}$ and (ii) localized to localized states for $T < T_{max}$ that dominate in type I photoconductors. The similar behaviour has also been reported by Mathew and Philip [27-28] in case of As-Sb-Se, Se-Ge-In and Ge-Se-Bi glassy system.

Main and Owen [29] has also found the similar behaviour of photoconductivity in case of amorphous As$_2$S$_3$. The well defined activation energies involved in the temperature dependence of photoconductivity suggests that the recombination centers are located at relatively discrete levels of localized states. Main and Owen [29] have interpreted their data on the basis of a simple four level model containing an electron trap and hole trap. To identify the origin of the gap states, which are responsible for recombination Street and Mott [24] and Mott et al. [30] postulated the model of the so called dangling bonds. Their first hypothesis was that the chalcogenide glasses contain a high number of frozen-in structural defects and the missing chalcogen atoms leaving broken or dangling bonds on other atoms could be the source of localized defect states.

Maxima in photoconductivity with temperature have been reported in As-Te and As-Se systems [31] and the Si-Te-As system [32] near room temperature whereas it was found to be absent in Te$_{85}$Ge$_{15}$ and Te$_{85}$Ge$_{10}$Sb$_5$ [9] and Sb$_{15}$Ge$_{10}$Se$_{75}$ [33].
To obtain information about density of traps, i.e., of localized states that can capture free charge carriers, and about the mechanism for the recombination of the excess carriers in chalcogenide glasses, the other property of particular interest is the dependence of $\sigma_{ph}$ on the intensity $F$ of the illumination, a dependence that is often expressed as $\sigma_{ph}$ being proportional to $F^\gamma$, at least for a limited range of $F$. Intensity dependence of photoconductivity in amorphous semiconductors has been studied by several workers. In the simplest systems, such as crystalline semiconductors with only a few sets of traps at discrete energies, one usually finds that the exponent $\gamma$ equals either unity, corresponding to monomolecular recombination mechanism [32, 34, 35], or 0.5 corresponding to bimolecular recombination [26, 34, 35]. However, in many amorphous semiconductors [36], intermediate values of the exponent $\gamma$ are found. The occurrence of such values has been extensively discussed and explained by Rose [37-38] in terms of continuous distribution of localized states which can act as recombination centers if the intensity of the incident light is suitable. He showed that the values of $\gamma$ between 0.5 and 1.0 will be obtained if the density of localized states varies exponentially with their energy, and this model has been used to interpret many experimental results by numerous researchers [36].

By changing the intensity of light one may cross over from one regime into the other in the simple case of band-to-band recombination [39]. Using an exponential distribution of gap states, rather than the discrete levels Arnoldussen et al. [40] showed that a $\gamma$ between 0.5 and 1.0 and independent of $F$ would result, unless, as was pointed out by Kastener and Monoroe [41] and Okamato et al. [42], defects with a negative correlation energy pin the Fermi level in which $\gamma=0.5$ to $\gamma=1.0$ transitions will be seen.

6.2.3 Transient Photoconductivity:

It is well known, when a semiconductor is illuminated with lights of wavelengths lying in the fundamental absorption region, the absorption of light quanta produces electron transitions from the valence band to the conduction band and consequently non-equilibrium electrons and holes are generated. Now, each non-equilibrium carrier, for example an electron, takes part in thermal motion and consequently while moving in a band it has a definite probability of meeting a hole and of recombining with it or, as it is sometimes expressed, of being captured by a hole.

In general, a given semiconductors may contain several “types” of holes (free holes in the valence band, holes localized at various impurity levels or structure defends levels, etc.) due to the presence of several types of holes the probability of an electron meeting of a given type in
proportional to the density of three holes and to the average relative velocity of motion of the
electron and the holes \( v_n \). If \( q_n \) denotes "capture cross section" (or "recombination cross section")
for the capture of an electron by holes of a certain type the density of which is \( p \), then obviously
the average time between two meetings of the electrons with these holes is

\[
\tau_n = \frac{1}{q_n v_n p} \quad \text{--------- (6.22)}
\]

Since each such meeting ends with the capture of the electron by a hole, the time \( \tau_n \) is
essentially the average electron lifetime before capture by of the given type. If the semiconductors
contains \( k \) "type" of hole which capture electrons, then for each of them the life time \( \tau_{nk} \) may be
introduced as

\[
\tau_{nk} = \frac{1}{p_k q_{nk} v_{nk}} \quad \text{--------- (6.23)}
\]

If there are several type of hole which capture electrons, and there densities, cross sections,
and average relative velocities of motion are \( p_k, q_{nk} \) and \( v_{nk} \) respectively, then the total number of
possible collisions per unit time with all types of hole is obviously given by the sum

\[
\sum_k p_k v_{nk} q_{nk} \quad \text{--------- (6.24)}
\]

Consequently, the effective electron life time is

\[
\tau = \frac{1}{\sum_k p_k v_{nk} q_{nk}} \quad \text{--------- (6.25)}
\]

or,

\[
\tau = \sum_k \frac{1}{\tau_{nk}} \quad \text{--------- (6.26)}
\]

Thus, complex process involving several type of "capture center" may be considered in terms of
effective recombination characteristics obtained by summation of the "reciprocal lifetimes."

Similarly for holes the average electron lifetime before capture by electrons of the given
types given by,

\[
\tau_{pk} = \frac{1}{n_k q_{pk} v_{pk}} \quad \text{--------- (6.27)}
\]
where $n_k$ is the density of electrons of a given type capable of capturing holes and $q_{pk}$ is the cross section for the capture of a hole by these electrons.

6.2.4 Recombination of Non-Equilibrium Carriers:
A. Linear Recombination:

In this case the rate of recombination (capture) is proportional to the first power of the non-equilibrium carrier density. This case is realized, for example, when there are holes of only one type, which recombine with the non-equilibrium electrons, and the density of these holes $p$ is very high and practically independent of the illumination. Then, the rate of recombination (capture) of electrons, equal to $\Delta n / \tau_n$, is directly proportional to the density. This case is called a linear recombination.

The change of non-equilibrium carrier density per unit time may be written in the following form:

$$\frac{d(\Delta n)}{dt} = \beta k I - \Delta n / \tau$$

Let us assume that the illumination of the sample with light of constant intensity begins at a time $t = 0$. Then, separating variables and integrating, using the initial condition $\Delta n = 0$ when $t = 0$, one obtains

$$\Delta n = \tau \beta k I (1 - e^{-t/\tau})$$

or as $t \to \infty$, $\Delta n = \tau \beta k I = \Delta n_{eq}$

If the sample is not illuminated, then in place of eq. (4.13), one can write

$$\frac{d(\Delta n)}{dt} = - \Delta n / \tau$$

If illumination of the sample ceased at a time $t = 0$ and that the non-equilibrium density reached the value $\Delta n = \Delta n_{eq} = \tau \beta k I$ as the result of illumination up to this time. Then,

$$\Delta n = \tau \beta k I e^{-t/\tau}$$

It is important to note that the "time constant" of the exponential curves is equal to the lifetime. This gives a simple method of determining $\tau$ directly from the relaxation curves in the case of linear recombination.

B. Quadratic Recombination:

In this case the rate of recombination is proportional to the square of the non-equilibrium carrier density. This happens, for example, when the density of equilibrium carriers is zero and on
ionization the electrons are transferred from a lower to an upper band; then the densities of non-equilibrium electrons and holes are equal and rate of recombination is proportional to \((\Delta n)^2\). This case is called quadratic recombination.

In this case, in the presence of illumination we have, instead of Eqs. (6.28),

\[
\frac{d(\Delta n)}{dt} = \beta k I - \gamma (\Delta n)^2 \tag{6.33}
\]

When illumination ceases, we have

\[
\frac{d(\Delta n)}{dt} = -\gamma (\Delta n)^2 \tag{6.34}
\]

Using the initial conditions, similar to the conditions in the linear recombination case, we find that on illumination with a square pulse of sufficient duration the relaxation curves of rise and decay of non-equilibrium density (conductivity) are given by the expression:

For rise

\[
\Delta n = (\beta k I / \gamma) \frac{1}{2} \tanh (\tau \beta k I) \tag{6.35}
\]

For decay

\[
\Delta n = (\beta k I / \tau) \frac{1}{2} \left[ \frac{1}{t (\tau \beta k I) + 1} \right] \tag{6.36}
\]

Now the rise and decay are no longer symmetrical in the contrast to the linear recombination case where the rise and decay curves are exponential with the same time constants. Here, the rise is described by a hyperbolic tangent, and the decay (when \(t\) is large) by a much slower hyperbola.

The average electron lifetime, in the present case, is:

\[
\tau = (\gamma \Delta p)^{-1} \tag{6.37}
\]

Since the quantity \(\Delta p\) (the density of holes in the lower band) itself depend on the intensity of light and on time (in the non-steady-state case), it is clear that \(\tau\) is also a variable quantity, which, however, has a definite meaning at any given moment.

6.2.5 Effect of Trapping:

If a material existed with no levels in the forbidden gap, then it would be strictly true that every excited carrier in the crystal would also be a free carrier. If a material existed with only recombination centers of the common type such that the majority carrier life time is much greater than the minority-carrier life time, then it would still be true that every excited majority carrier would be a free carrier. If, however, as is the case in almost all real materials, there are also
trapping centers as well as recombination centers, the number of free carriers may be less than the number of excited carriers.

One of the ways of considering this effect of trapping is to define a "drift mobility" \( \mu_d \). The conductivity, actually observed, for the true density of free carriers moving with the mobility of free carriers, is equal to the conductivity that would be expected if all the excited carriers moved with the drift mobility. Then we may write:

\[
(\ n + n_t\ ) \mu_d = n \mu
\]

where \( n_t \) is the density of trapped carriers, and we consider just the contribution from the majority carriers, it follows that

\[
\mu_d = \left[ \frac{n}{n + n_t}\right] \mu
\]

Frequently, at least in insulators, \( n_t >> n \),

\[
\mu_d = \left( \frac{N_e}{N_1}\right) \exp(-E_t/RT) \mu
\]

where \( E_t \) is the depth of the levels associated with the trapping centers, i.e., the energy separation between the bottom of the conduction band and the levels, \( N_1 \) is the density of trapping centers and \( N_e \) is the effective density of states in conduction band.

A majority effect of trapping is to make the experimentally observed decay time of the photocurrent, after the excitation has ceased, longer than the carrier lifetime. If no trapping centers are present, then the observed photocurrent will decay in the same way as the density of free carriers, and the observed decay time will be equal to the carrier lifetime. If trapping centers are present, but the free-carrier density is much greater than the density of trapped carriers, again the observed decay time of the photocurrent will be equal to the carrier lifetime. But, when the density of free carriers is comparable to or less than the density of trapped carriers, the thermal freeing of trapped carriers during the course of the decay can prolong the decay. In such a case, the observed decay time is longer than the actual recombination determined lifetime of a free carrier. In the extreme case, when the density of trapped carriers is much greater than the density of free carriers, the entire decay of photocurrents is effectively dominated by the rate of trap emptying rather than by the rate of recombination. In addition to making the observed decay time longer than the lifetime of a free carrier, the presence of traps may also decrease the sensitivity of a photoconductor.

As described above, the variation of \( n \) as \( F^{1/2} \) (where \( F \) is the intensity of light) expected for a trap-free material, is changed to a linear variation of \( n \) with \( F \) for a material with an uniform distribution of traps. A variation of \( n \) as \( F^{1/2} \) can be found even with trapping, however, if the
density of photoexcited electrons trapped above the electron Fermi Level is greater than the density of photoexcited electrons trapped below the Fermi Level. The experimental observation of a variation of \( n \) with a power of \( F \) between \( 1/2 \) and 1 can be described by assuming an exponential distribution of traps, i.e., the density of traps of energy \( E_t \) decreasing exponentially with the distance \( E \) from the bottom of the conduction band. Thus, in the range of light intensities for which the density of free carriers is less than the density of trapped carriers, this simple model provides description for \( n \) varying with power of \( F \) between 0.5 and 1. For high light intensities, such that the density of free carriers is greater than the density of trapped carriers, bimolecular recombination will predominate and \( n \) will vary as \( F^{1/2} \).

The present chapter reports the steady state and transient photoconductivity measurements in amorphous thin films of \( \text{Se}_{80-x}\text{Te}_{20}\text{Cd}_x \) (\( x = 0, 5, 10 \) and 15) and \( \text{Se}_{80-x}\text{Te}_{20}\text{Ag}_x \) (where \( x = 0 \) and 4) prepared by vacuum evaporation technique. The above mentioned theory has been applied to interpret the data observed. Temperature dependence of steady state photoconductivity is studied at different light intensities. Intensity dependence of photoconductivity is studied at different fixed temperatures. Composition dependence of various photoconductive parameters is also discussed. The rise and decay of photoconductivity have also been studied in the samples at various intensities and illumination times at room temperature. To measure the rise and decay of photoconductivity with time, thin film sample was mounted in the same metallic sample holder and light of desired wavelength was shown through a transparent window. After a certain time of exposure, the light was turned off and the decay of current was measured as a function of time. The results have been presented and discussed in next sections. The conclusions have been presented in the last.

**Procedure of measurements:**

The electrical conductivities in dark as well as in presence of light were studied by mounting samples in a specially designed sample holder, in which the illumination could be achieved through a transparent window in a vacuum of \( 10^{-2} \) Torr. The source of light is a 200 Watt. tungsten lamp. The intensity of light was varied by changing the voltage across the lamp. The intensity is measured by a lux meter (Testron model LX - 101). A dc voltage was applied across the film and the resulting current is measured by a digital electrometer (Keithley, model 6517A). I-V characteristics are found to be linear and symmetric up to 30 volts in samples studied. The heating rate is kept quite small (0.5 K/min) for these measurements. The temperature of the film
was controlled by mounting a heater inside the sample holder, and measured by a calibrated copper-constantan thermocouple mounted very near to the film.

6.3 Steady State and Transient Photoconductivity in a-Se$_{80-x}$Te$_{20}$Cd$_x$ Thin Films:

6.3.1 Temperature and Composition Dependence of Dark Conductivity:

Glassy alloys of Se$_{80-x}$Te$_{20}$Cd$_x$ ($x = 0, 5, 10$ and $15$) and their thin films have been prepared as stated in previous chapter-2. Procedure of measurements and the sample holder used in the present study are same as discussed in previous chapters.

Fig. 6.1 shows the temperature dependence of dark conductivity ($\sigma_d$) for pure and Cd-doped Se$_{80}$Te$_{20}$ binary alloys. It is clear from this figure that ln $\sigma_d$ vs 1000/T curves are straight lines, indicating that the conduction in these glasses is through an activated process having a single activation energy in the temperature range 300K to 340K. The d.c. conductivity ($\sigma_d$) can, therefore, be expressed by the usual relationship

$$\sigma_{dc} = \sigma_0 \exp \left(-\frac{\Delta E}{kT}\right)$$

(6.41)

Where $\Delta E$ is called the activation energy for d.c. conduction, $\sigma_0$ is called the pre-exponential factor and $k$ is Boltzmann’s constant.

The values of $\Delta E$ were calculated for various samples using the slopes of the curves of Fig. 6.1. These values are listed in Table 6.1. The values of $\sigma_d$ at room temperature (300 K) are also given in Table 6.1. Figs. 6.2-6.3 plot the values of $\sigma_{dc}$ (at 300 K) and $\Delta E$ as a function of the Cd concentration. It is clear from these figures that $\sigma_{dc}$ increases and $\Delta E$ decreases with increasing Cd concentration.

An increase in $\sigma_{dc}$ with a decrease in $\Delta E$ may be associated with the decrease of the mobility gap upon increasing Cd concentration in the Se$_{80-x}$Te$_{20}$Cd$_x$ glassy system. The value of $\sigma_0$ also decreases as the Cd concentration increases, which indicates that the density of localized states (DOS) may be affected by Cd incorporation.

6.3.2 Temperature and Composition Dependence of Steady State Photoconductivity:

The thermally activated dc conduction is a common feature of chalcogenide glasses due to their semi-conducting nature. In presence of light, Fermi level splits into quasi Fermi levels and
move towards valence band for holes and towards conduction band for electrons. The position of these quasi Fermi levels depends on light intensity \([43]\). The activation energy therefore becomes smaller in presence of light as compared to in dark.

Fig. 6.4 shows the temperature dependence of photoconductivity \((\sigma_{ph})\) at a particular intensity \((13000\ \text{lux})\). It is clear from this figure that \(\sigma_{ph}\) increases with increasing temperature in the temperature range of the present measurements. At a particular temperature \(\sigma_{ph}\) increases as the Cd concentration increases. This is shown in Fig. 6.5. A similar variation was also observed in the dark conductivity (see Fig. 6.2.).

The important parameter in photoconductivity measurements is the photosensitivity \((\sigma_{ph}/\sigma_d)\) at a particular temperature and intensity. The value of \(\sigma_{ph}/\sigma_d\) for a particular material determines the use of that material in photoconductive devices. We have therefore calculated \(\sigma_{ph}/\sigma_d\) at various temperatures for all of the samples at a particular intensity \((13000\ \text{lux})\). The values of \(\sigma_{ph}/\sigma_d\) at room temperature are given in Table 6.1 and plotted in Fig. 6.6 as a function of \(x\) in \(\text{Se}_{80-x}\text{Te}_{20}\text{Cd}_x\) glassy system. It is clear from this figure that an appreciable reduction in \(\sigma_{ph}/\sigma_d\) is observed at room temperature. Similar results were also obtained at other temperatures.

6.3.3 Temperature and Composition Dependence of Transient Photoconductivity:

To measure the rise and decay of photoconductivity with time, thin film samples were mounted in the same metallic sample holder and light of desired wavelength was shown through a transparent window. After a certain time of exposure, the light was turned off and the decay of current was measured as a function of time. The initial dark value of current was subtracted to obtain photoconductivity during decay.

Figs. 6.7-6.10 show the results of the transient photoconductivity measurements in all the samples. It is clear from fig.6.7 that the rise of the photocurrent shows an anomalous behavior in case of \(\text{Se}_{80}\text{Te}_{20}\) binary glassy alloy. The photocurrent passes through a maximum before attaining the steady state. The same kind of the results has also been reported previously by some other groups \([44-45]\). The results indicate that the anomalous behavior increases as the steady state photocurrent increases at higher intensities or higher temperatures. This anomalous behavior could be understood in terms of non-equilibrium recombination as suggested by them. Our results are also in agreement with their results. However, the aforesaid behavior could not be observed by us.
in any Cd doped composition chosen in the present study. This could be due to enhance in the density of defect states with Cd concentration.

Figs. 6.8-6.10 show the results of the transient photoconductivity measurements in Cd doped samples. It is clear from these figures that the rise and decay of photocurrent is quite slow in all the samples. A persistent photocurrent (the asymptotic value of the current in the decay curve) was also observed in all the samples. This type of decay of photocurrent was observed [46-47] in various kinds of chalcogenide glasses. To simplify the analysis, we have subtracted the persistent photocurrent from the measured photocurrent and found that the decay of photocurrent is non-exponential even after subtracting the persistent photocurrent. The slower decay after incorporation of Cd in binary Se_{80}Te_{20} glassy alloy shows that the density of defect states increases with increase in percentage of Cd in the present glassy system.

**Table: 6.1**

Electrical Parameters in a- Se_{80-x}Te_{20}Cd_{x} Thin Films

<table>
<thead>
<tr>
<th>Glassy Alloys</th>
<th>$\sigma_d$ ($\Omega^{-1} \text{ cm}^{-1}$) at 300K</th>
<th>$\Delta E$ (eV)</th>
<th>$\sigma_{ph}$ ($\Omega^{-1} \text{ cm}^{-1}$) at 300K</th>
<th>$\sigma_{ph} / \sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se_{80}Te_{20}</td>
<td>2.50 X 10^{-9}</td>
<td>0.44</td>
<td>1.19 X 10^{-7}</td>
<td>47.6</td>
</tr>
<tr>
<td>Se_{75}Te_{20}Cd_{5}</td>
<td>2.58 X 10^{-8}</td>
<td>0.43</td>
<td>2.08 X 10^{-7}</td>
<td>8.1</td>
</tr>
<tr>
<td>Se_{70}Te_{20}Cd_{10}</td>
<td>1.04 X 10^{-6}</td>
<td>0.42</td>
<td>2.46 X 10^{-6}</td>
<td>2.4</td>
</tr>
<tr>
<td>Se_{65}Te_{20}Cd_{15}</td>
<td>7.50 X 10^{-6}</td>
<td>0.40</td>
<td>1.70 X 10^{-5}</td>
<td>2.3</td>
</tr>
</tbody>
</table>

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Figure 6.1: Temperature dependence of dark conductivity in $\text{Se}_{80-x}\text{Te}_{x}\text{Cd}_2$ thin films
Figure 6.2: Composition dependence of dark conductivity at 300 K in $\text{Se}_{80-x}\text{Te}_{20}\text{Cd}_x$ thin films.
Figure 6.3: Composition dependence of Activation Energy in Se$_{80-x}$Te$_{20}$Cd$_x$ thin films
Figure 6.4: Temperature dependence of the photoconductivity in $\text{Se}_{80-x}\text{Te}_{20}\text{Cd}_x$ thin films
Figure 6.5: Composition dependence of photoconductivity at 300 K in $\text{Se}_{80-x}\text{Te}_{20}\text{Cd}_x$ thin films.
Figure 6.6: Composition dependence of photosensitivity at 300K in $\text{Se}_{80-x}\text{Te}_{20}\text{Cd}_x$ thin films.
Figure 6.7: Time dependence of photocurrent at different intensities during rise and decay at 300 K in Se$_{80}$Te$_{20}$ thin film
Figure 6.8: Time dependence of photocurrent at different intensities during rise and decay at 300K in Se$_{75}$Te$_{20}$Cd$_{5}$ thin film.
Figure 6.9: Time dependence of photocurrent at different intensities during rise and decay at 300K in Se$_{70}$Te$_{20}$Cd$_{10}$ thin film.
Figure 6.10: Time dependence of photocurrent at different intensities during rise and decay at 300K in Se$_{65}$Te$_{20}$Cd$_{15}$ thin film.
6.4 Steady State and Transient Photoconductivity in a-Se$_{80-x}$Te$_{20}$Ag$_x$ Thin Films:

6.4.1 Temperature Dependence of Dark and Photoconductivity:

Glassy alloys of a-Se$_{80-x}$Te$_{20}$Ag$_x$ (where x = 0 and 4) and their thin films have been prepared as stated in previous chapter-2. Procedure of measurements and the sample holder used in the present study are same as discussed in previous chapters.

Figs. 6.11 and 6.12 show the temperature dependence of dark conductivity and steady state photoconductivity at different intensities (F) for Se$_{80}$Te$_{20}$ and Se$_{76}$Te$_{20}$Ag$_4$ respectively. It is clear from these Figs. that ln $\sigma$ vs. $1000/T$ curves are straight lines having single slope indicating that the dark conductivity as well as photoconductivity is due to an activated process having single activation energy in the present range of temperature. The conductivity can, therefore, be written as Eq. 6.41 given above.

The values of $\Delta E$ are calculated using the slopes of Figs. 6.11 and 6.12 and Eq.6.41. The results of these calculations are given in Table 6.2. It is clear from this Table that the activation energy decreases with Ag impurity. Also 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.

6.4.2 Intensity Dependence of Photoconductivity:

Intensity (F) dependence of photoconductivity ($\sigma_{ph}$) is studied at different temperatures. The results for Se$_{80}$Te$_{20}$ and Se$_{76}$Te$_{20}$Ag$_4$ glassy alloys are shown in Figs. 6.13 and 6.14 respectively. It is clear from these Figs. that at all temperatures, ln $\sigma_{ph}$ vs. ln F curves are nearly straight lines which indicate that photoconductivity follows a power law with intensity ($\sigma_{ph} \propto F^\gamma$).

6.4.3 Transient Photoconductivity:

The rise and decay of photoconductivity have also been studied in both the samples at various intensities and illumination times at room temperature. To measure the rise and decay of photoconductivity with time, thin film sample was mounted in the same metallic sample holder and light of desired wavelength was shown through a transparent window. After a certain time of exposure, the light was turned off and the decay of current was measured as a function of time.

Figs. 6.7 and 6.15 show the results of the transient photoconductivity measurements at different intensities in Se$_{80}$Te$_{20}$ and Se$_{76}$Te$_{20}$Ag$_4$ glassy alloys. It is clear from these figures that the rise of the photocurrent with time shows an anomalous behavior. At lower intensities, the
photocurrent rises monotonically to the steady state value. Such type of rise of photocurrent is common in chalcogenide glasses and we, therefore, call it a normal behavior. However, at higher intensities, the rise is quite different. The photocurrent passes through a maximum value before attaining the steady state value. We call this behavior anomalous. The results indicate that the anomalous behavior increases as the steady state photocurrent increases at higher intensities or higher temperatures.

Table: 6.2

Photoelectrical Parameters in a-\(\text{Se}_{80-x}\text{Te}_{20}\text{Ag}_x\) Thin Films

<table>
<thead>
<tr>
<th>Glassy Alloys</th>
<th>(\sigma_d) ((\Omega^{-1}\text{cm}^{-1})) at 300K</th>
<th>(\sigma_{ph}) ((\Omega^{-1}\text{cm}^{-1})) at 300K</th>
<th>(\sigma_{ph}/\sigma_d)</th>
<th>(\Delta E) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Se}<em>{80}\text{Te}</em>{20})</td>
<td>(2.50 \times 10^{-9})</td>
<td>(1.19 \times 10^{-7})</td>
<td>47.6</td>
<td>0.44</td>
</tr>
<tr>
<td>(\text{Se}<em>{76}\text{Te}</em>{20}\text{Ag}_4)</td>
<td>(1.25 \times 10^{-7})</td>
<td>(4.34 \times 10^{-6})</td>
<td>34.7</td>
<td>0.43</td>
</tr>
</tbody>
</table>
Figure 6.11: Temperature dependence of dark and photoconductivity at different intensities in Se$_{80}$Te$_{20}$ thin film.
Figure 6.12: Temperature dependence of dark and photoconductivity at different intensities in Se$_{76}$Te$_{20}$Ag$_4$ thin film.
Figure 6.13: Intensity dependence of photoconductivity at different temperatures in Se$_{80}$Te$_{20}$ thin film
Figure 6.14: Intensity dependence of photoconductivity at different temperatures in Se$_{76}$Te$_{20}$Ag$_4$ thin film
Figure 6.15: Time dependence of photocurrent at different intensities during rise and decay at 300 K in \( \text{Se}_{76}\text{Te}_{20}\text{Ag}_4 \) thin film.
As suggested by Andrish et al. [48] this anomalous behavior could be understood in terms of non-equilibrium recombination in the high intensity region where bimolecular recombination takes place. At lower intensities where monomolecular recombination may take place, these maxima may be absent and photocurrent rises monotonically to the steady state value. At intermediate intensities, a transition from monomolecular to bimolecular recombination may take place as time increases. Because of the quasi-stationary state near the maxima, the maxima may not be very sharp at intermediate intensities.

In the present case also, the anomalous rise of photocurrent is observed at higher intensities only. At much lower intensities, the anomalous behavior is not observed at all. The anomalous effect increases as the intensity of light increases. These results are in accordance with the theory of Andrish et al. Another explanation of the anomalous rise of photocurrent can be given in terms of structural relaxation processes which may affect the physical parameter near the glass transition temperature. The structural relaxation rate depends on the annealing temperature and also on whether light is shining. One can argue that, near the glass transition temperature, the relaxation rate that is obtained when light is shining becomes so large that the defects start equilibrating on the time scale of the present measurements. The observed anomalous rise in the photocurrent may thus be a consequence of light and temperature-induced structural relaxation effects.

Non-exponential decay with quite slow decay rate has been observed. Transient photoconductivity measurements at different intensities indicate that the decay of photoconductivity has two components; initially; it is little faster 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.

6.5 Conclusions:

Temperature (300K-340K) and composition dependence of conductivity is studied in dark and in presence of light in amorphous thin films of Se$_{80-x}$Te$_{20}$Cd$_x$ ($x = 0, 5, 10$ and $15$), prepared by vacuum evaporation technique. These measurements at different intensities indicate that the dark conductivity as well as photoconductivity both is thermally activated in the above temperature range in all the samples studied. 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.

The present measurements also indicate that the photosensitivity \( \sigma_{\text{ph}} / \sigma_d \) decreases on increase in Cd concentration in this glassy system. This indicates that the density of defect states must be larger for samples containing higher and higher concentration of Cd.

Transient photoconductivity measurements have been also studied in all the glassy samples. It has been observed that the rise of the photocurrent shows an anomalous behavior in case of Se80Te20 binary glassy alloy only which could not be observed in any ternary compositions. This anomalous behavior could be understood in terms of non-equilibrium recombination. Non-exponential decay with quite slow decay rate has been observed, in the other samples which indicates the increase of density of defect states with increasing content of Cd in the present glassy system.

Temperature and intensity dependence of conductivity is studied in dark and in presence of light in thin films of Se_{80-x}Te_{20}Ag_x prepared by vacuum evaporation technique. The values of \( \Delta E \), \( \sigma_d \), \( \sigma_{\text{ph}} \), and \( \sigma_{\text{ph}}/\sigma_d \) are calculated. It has been observed in present study that \( \sigma_d \) and \( \sigma_{\text{ph}} \) increases while \( \Delta E \) and \( \sigma_{\text{ph}}/\sigma_d \) decreases with Ag impurity. These measurements at different intensities indicate that the dark conductivity as well as photoconductivity both is thermally activated in the above temperature range in all the samples studied. 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 have been also studied in both the glassy samples. An anomalous behavior in the rise of the photocurrent is observed which could be understood in terms of non-equilibrium recombination as suggested by Andrisch et al. The decay is found to be non-exponential in the present case indicating the presence of continuous distribution of defect states.
References:


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