CHAPTER - 1

AN INTRODUCTION TO AMORPHOUS/GLASSY SEMICONDUCTORS AND SELECTION OF THE PROBLEM
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1.1. A Brief History of Amorphous/Glassy Semiconductors

A glassy state is continuous with an analogous to the liquid state of that substance which has attained a high viscosity due to rapid cooling from the melt. By definition, therefore, only those solids, which are made non-crystalline by rapid cooling from the melt, are termed as glasses. Glass is one of the earliest creation of the mankind. Perhaps, no other material posses so unique combination of physical and chemical properties such as transparency, ability to withstand high temperatures, a good mechanical strength and low cost etc.

All the glasses known before 1955, e.g. silicate, phosphate and borate glasses were insulators in the sense that electronic conduction was absent in these glasses. Though some of these glasses may have appreciable conductivity particularly in impure state, even then they are not termed as semiconductors because conduction in them is ionic rather than electronic. Because of the absence of electronic conduction, these glasses could not be used in solid state devices unlike their crystalline counterpart where electronic conduction does exist. The theory of semiconductor was also
based on the periodicity of atoms in solids. So, for a very long time, it was thought that non-crystalline solids could not be semiconductors.

In 1955, however, B.T. Kolomiets and his associates, in USSR, first used sixth group elements (S, Se, Te) instead of conventional elements 'O' which was used to prepare glasses at that time. A special name 'Chalcogenide Glasses' was given to these glasses. Kolomiets et. al. [1] did not find these materials very interesting as they could not make n- or p-type semiconductors by adding conventional doping elements of V or III groups.

A much stimulating work on these glasses started after Ovshinsky who reported [2] two types of switching phenomena in these glasses. Since then, the application of these glasses, either realized or anticipated, include a very wide spectrum. These materials have found application in optical recording devices, optical mass memories, image converters and intensifiers, switching and memory devices, continuous dynode electron multipliers, phase contrast holograms, high energy particle detectors, infra-red lens, ultrasonic delay lines and microfiche transparencies etc. In addition to these they have the exciting applications in xerography also. The high conductivity of these glasses and the absence of ionic conduction in them, led scientists to study their electrical and physico-chemical properties. Further, the advantage of preparing these glassy semiconductors in thin films form makes them adaptable to integration with other solid state technologies.
1.2. Classification of Amorphous/Glassy Semiconductors

It was Joffe [3] who first pointed out that the basic electronic properties of a solid are determined primarily by the character of the bonds between nearest neighbors rather than by the long range order. Long range order is completely absent in amorphous semiconductors though they can have short range order up to a few atomic dimensions.

According to the differences in chemical bonding, amorphous semiconductors may be grouped into three major categories as given below:

1) Covalently Bonded Amorphous Semiconductors
   a) Tetrahedral Amorphous Films
      Si, Ge, SiC, InSb, GaAs, GaSb ....
   b) Tetrahedral Glasses, $A^{II} B^{IV} C_{2}^{V}$
      Cd Ge$_x$ As$_2$, Cd Si$_x$ P$_2$, Zn Si$_x$ P$_2$, Cd Sn$_x$ As$_2$ ....
   c) Lone Pair Semiconductors (Chalcogenide glasses)
      I) Elements and Compounds
         Se, S, Te, As$_2$Se$_3$, As$_2$S$_3$ ....
      II) Cross-Linked Networks
         Ge-Sb-Se          Se-Ge-As-Te
         Ge-As-Se          As$_2$Se$_3$- As$_2$Te$_3$
         As-Se-Te          Te$_2$Se$_3$- As$_2$Te$_3$
2) Semiconducting Oxide Glasses

\[
\begin{align*}
V_2O_5 - P_2O_5 & \quad \text{MnO-Al}_2\text{O}_3-\text{SiO}_2 \\
V_2O_5 - P_2O_5-\text{BaO} & \quad \text{CoO-Al}_2\text{O}-\text{SiO}_2 \\
V_2O_5 - \text{GeO}_2-\text{BaO} & \quad \text{FeO-Al}_2\text{O}_3-\text{SeO}_2 \\
V_2O_5 - \text{PbO-Fe}_2\text{O}_3 & \quad \text{TiO}_2-V_2\text{O}_3-\text{BaO} \\
\end{align*}
\]

3) Dielectric Films

\[
\text{SiO}_x , \text{Al}_2\text{O}_3 , \text{ZrCO}_2 , \text{Ta}_2\text{O}_3 , \text{Si}_3\text{N}_4 , \text{BN}, \ldots .
\]

The first group contains (a) the tetrahedral semiconductors which can only be prepared by thin film deposition (b) tetrahedral glasses and (c) the lone pair semiconductors. The name of this class of materials stems from the fact that their properties are primarily influenced by the two non bonding p-orbitals of the groups VI chalcogen elements in two fold co-ordination [4]. As they contain chalcogen elements in large proportions, they are also known as chalcogenide glasses.

The second main group contains the oxide glasses, which have strong ionic bonds and are usually good insulators but which can be made semiconductor by the addition of the transition metal ions in different valance states. The conduction process then proceeds via a charge exchange among the valence transition metal ions.

The third group contains the dielectric films sensitive to disorder as their electronic conduction relies on deviation from stoichiometry and the presence of defect centers, which act as donors and acceptors. According to
Joncher [5] and Hill [6], the electronic properties of these films distinguish them from the covalent amorphous solids.

Out of the three types of glassy semiconductors (tetrahedral glasses, chalcogenide glasses and oxide glasses), chalcogenide glasses have gained much importance because of their potential application in various solid state devices mentioned earlier. The present thesis, therefore, deals only with the defect controlled electrical properties of chalcogenide glasses, i.e., the category (1 c) in classification table mentioned above.

1.3. Preparation of Amorphous/Chalcogenide Glassy Semiconductors

(i) Quenching Technique

In this technique, materials are prepared in glassy form by rapid cooling of the melt. For the preparation of glasses the required composition is prepared by weighing the constituent elements in desired atomic percentages and then sealed in quartz ampoules with a high vacuum $\sim 10^{-5}$ Torr. These ampoules are kept in a furnace at a temperature so that all the components get melted. The sealed ampoules are frequently rocked for about ten hours to make the melt homogeneous. The quenching is done by dropping the quartz ampoules suddenly in ice cooled water or liquid nitrogen, depending upon the requirement. In some cases, air quenching is sufficient, where air is blown on the heated ampoules by an air blower.
(ii) **Thermal Evaporation Technique**

In this technique, the materials are made amorphous in the form of thin films by creating high vacuum in the Bell Jar and heating the filament containing the material, by passing current in it. The substrate used may be glass or any other suitable material. Substrate temperature can also be varied by mounting a heater inside the bell jar. Standard coating units are available in the market for making thin films by this technique.

(iii) **Flash Evaporation Technique**

This technique is similar to the technique described above except that the material is dropped on already heated filament instead of heating the filament along with the material. The fractionation effect is reduced in this technique. In addition to the coating unit used above a small a.c. magnetic field is established to produce vibration in a magnetic strip containing material.

(iv) **Sputtering Technique**

In essence, it consists of the bombardment of a target by energetic ions from low pressure plasma, causing erosion of materials, either atom by atom or as clusters of atoms and subsequently depositing of film on the substrates. The simplest way to induce sputtering is to apply a high negative voltage to the target surface, thereby attracting positive ions from the plasma. However, the d.c. sputtering process is feasible only when target is sufficiently conducting so that target can act as electrode.
In case of insulating materials, a common approach is to apply an r.f. field to the target. For this purpose, all that is required is for the r.f. voltage to be capacitively coupled to the target surface. For metallic targets, this is achieved by connecting a capacitor in series with the target, insulating targets are normally bonded to a metal backing electrode, which acts as a capacitive component. The material deposited on the substrate can form amorphous films for the same reason as in evaporation.

1.4 Electronic Structure of Amorphous/Glassy Semiconductor

According to Mott [7], the spatial fluctuations in the potential, caused by the configurational disorder in amorphous materials may lead to the formation of localized states. The states are called localized because an electron placed in a region will not diffuse to other regions at zero temperature with corresponding potential fluctuations. Based on the Anderson theory [8], Mott [9] proposed that localized states do not occupy all the energies in the band.

Fig. 1.1 (a) shows the CFO model [10] in which the tail states extend across the gap. The continuous decrease of localized states destroys the sharpness of valance and conduction band edges. Later, a similar model was proposed by Spear [11] to evaluate barrier formation in amorphous Si. He suggested that, in chalcogenide glasses, the disorder might be so great that tail of valence and conduction bands overlap. Due to large distortions, there would be a sufficient amount of density of states in the
Fig. 1.1
middle of the gap. Due to overlapping of the bands there are states in the valance band, ordinarily filled, which have higher energies than the conduction band that are ordinarily unfilled. A redistribution of electrons takes place, forming filled states in the conduction band tail which are negatively charged, and empty states in the valance band tail which are positively charged. This model ensures self-compensation and pins the Fermi level close to the middle of the gap, a feature required by the electrical properties of the materials. One of the major objections of this model is the high transparency in IR region of these materials below a well-defined absorption edge.

Davis and Mott [12] proposed that the tails of localized states should be narrow and should extend a few tenths of an electron volt into the forbidden gap. They also proposed the existence of a band of compensated levels near the middle gap, originating from defects in the random network, e.g., dangling bonds, vacancies. Fig.1.1 (b) shows the Davis-Mott model, here $E_e$ and $E_v$ represent the energies, which separate the ranges where the states are extended and localized. The center band may split into a donor and acceptor band, which will also pin the Fermi level (Fig. 1.1 (c)). It was suggested by Mott that at the transition from extended to localized states the mobility drops by several order of magnitudes producing a mobility edge. The energies at $E_e$ and $E_v$ act as a pseudogap and is defined as a mobility gap. It was proposed by Cohen [13] that there should not be an abrupt
change but a rather continuous drop of the mobility edge in this range. The mean free path of carriers is just equal to the inter-atomic distances so that ordinary transport theory based on Boltzmann's equation can not be used.

A model showing bands of donors and acceptors in the upper and lower halves of the mobility gap, has been introduced by Marshall and Owen [14]. It is clear now that the density of states of a 'real' amorphous semiconductor does not decrease monotonically into the gap but shows many peaks which can be well separated from each other, as in the case of chalcogenide glasses. The position of the Fermi level is largely determined by the charge distribution in the gap states. Fig. 1.1 (d) illustrates such a picture for the density of state distribution for glassy As₂Se₃ [15].

Emin [16] introduced the concept of polaron and discussed its applicability to amorphous materials via the utilization of a short-range. He argued that the presence of disorder tends to constrain a carrier's motion, thereby making small polaron formation generally easier in disordered materials than its crystalline counterpart. The slowing down may lead to a localization of the carrier and if the carrier stays at an atomic site sufficiently long enough for atomic re-arrangements to take place, it may induce displacements of the atoms in its immediate vicinity, causing small polaron formation. Since the small polaron is local in nature, the absence of long range order in non-crystalline solids may be expected to have no significant influence on its motion. In support of the validity of his ideas, Emin was able
to analyze experimental data of dc conductivity, thermo-power and Hall-mobility obtained on some chalcogenide glassy systems in the framework of the existing polaron theories developed for crystalline solids.

1.5 **Chemical Bond Description and Defects in Chalcogenide Glasses:**

In covalent bonded amorphous semiconductors the co-ordination environment can adjust itself to satisfy the valence requirements of each atoms in such a way that shallow donors or acceptors are not likely to occur in amorphous semiconductors [17]. Fig (1.2 a) shows the origin of electronic states in the two classes of amorphous semiconductors (a) tetrahedral semiconductors and (b) semiconductors containing group VI elements in two fold co-ordination.

Ge in four fold co-ordination has hybridized $sp^3$ orbitals. These are splitted into bonding ($\sigma$) and anti bonding ($\sigma^*$) states which the valance and conduction band respectively form in tetrahedral semiconductors. In Se, only two of the three p- states are utilized for bonding when the chalcogen is in two fold co-ordination. This leaves one non-bonding electron pair. As shown in Fig (1.2 b), in solid Se, these lone pair (LP) electrons form a band near the original p- state energy. The $\sigma$ and $\sigma^*$ bands are splitted symmetrically with respect to this reference energy. The higher lying filled LP band is the valance band in these materials [18]. In LP semiconductors the occupied state from $\sigma$ falls into the LP band and the acceptor some what above it.
Fig. 1.2-a

Fig. 1.2-b
The LP state of other Group VI elements form donors if they fall above the LP band of the host chalcogenide. The energy of LP states depends on the chemical environment. The addition of electropositive elements to LP semiconductors raises some LP states as localized donor states into the gap, thus producing or broadening the valence band tail. On the other hand, when a strongly electropositive atom like Cu or Cd is added to glassy semiconductor, say As$_2$Se$_3$, strongly bonded copper or cadmium selenide is formed, and as a result the number of As-As bonds is increased.

In an amorphous covalent material the local co-ordination environment is not fixed by long range order which causes the very different effects of impurities on the electronic properties of glasses. It appears that one cannot shift the Fermi-level close to either band. The Fermi level remains in the center region of the gap in the glasses, approximately in the central part of the gap.

Let us now discuss the nature of the defects responsible for the various physical properties of chalcogenide glasses. Here, the original proposals of Street et.al. [19,20] and Kastner et.al. [21,22] will be discussed in brief. Both of these proposals are based on the important idea proposed by Anderson [23]. According to him, in amorphous semiconductors, there is a strong tendency for electrons to be paired in bonding configuration, the coulomb repulsion between electrons at the same site being out weighed by a negative
term in the energy due to electron phonon interaction which leads configuration changes in the local atomic structure.

The absence of ESR signal and $T^{-1/4}$ hopping conduction in chalcogenide glasses (except from film deposited at low temperatures [24]) requires that no single-spin centers be present. Therefore, Anderson's proposal seems in a good agreement with the experimental results. Street and Mott [19] and Mott, Davis and Street [20], therefore, choose to apply the Anderson negative $U_{\text{eff}}$ concept to specific defects in an otherwise fully connected network. Let us now discuss this model, taking the example of selenium.

Consider the two dangling bonds at the ends of the selenium chain illustrated in Fig. 1.3 (a). When each contains a single electron the defects are neutral and will be designated $D^0$. Transfer of an electron from one chain end to other will lead to the creation of two charged defects $D^+$ and $D^-$. It is proposed that the reaction

$$2D^0 \rightarrow D^+ + D^-$$

is exothermic, the necessary lowering in energy arising from local lattice distortions.

On a configurational co-ordinate diagram [Fig. 1.3 (b)], the positive correlation energy $U$ associated with the two electrons at $D^-$ in the absence of configurational changes becomes negative ($U_{\text{eff}}$) after lattice relaxation.
Fig. 1.3
The chemical reason for the exothermic nature of the reaction is that, at $D^+$, an extra bond with a neighbouring chain can be formed by utilizing the normally non-bonding lone pair electrons. The co-ordination of Se atoms at $D^+$ is therefore three, at $D^-$ it is one, at a normally bonded Se atom where it is two. MDS proposed that the lattice distortion at $D^-$ is negligible, at $D^+$ it is considerable and at $D^0$ it is intermediate.

Kastner et.al. [21,22] have given a chemical bond description of these and represented the charged states of the defect as $C^-_1$ and $C^+_3$, $C$ standing for chalcogenide and the subscript indicating the atomic co-ordination. $C^0_3$ is labeled as neutral center because these authors believe that an extra electron placed on $C^+_3$ is shared equally between the three bonds of the atom, which therefore remains three fold coordinated. This description is quite different than that proposed by Street and Mott (19) and MDS [20] for neutral center, in which it was proposed that the extra electron be localized primarily on only one of the three bonds.

The structure and energies of several bonding configurations for a chalcogen are displayed in Fig.1.4. The normal bonding configuration is $C^0_2$, the straight lines representing bonds ($\sigma$ states) and the dots the lone pair (LP), and non-bonding electron. In this configuration, the anti-bonding ($\sigma^*$) states are empty and the energy relative to LP level, is $-2E_b$ as shown. Anti-
<table>
<thead>
<tr>
<th>Configuration</th>
<th>p-level occupation</th>
<th>Energy/configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2^0$</td>
<td>$\sigma^*$</td>
<td>$-E_b + \Delta$</td>
</tr>
<tr>
<td>$C_3^0$</td>
<td></td>
<td>$-2E_b + \Delta$</td>
</tr>
<tr>
<td>$C_3^-$</td>
<td></td>
<td>$-3E_b$</td>
</tr>
<tr>
<td>$C_3^-$</td>
<td></td>
<td>$-E_b + 2\Delta + U_{\sigma^*}$</td>
</tr>
<tr>
<td>$C_1^0$</td>
<td></td>
<td>$-E_b$</td>
</tr>
<tr>
<td>$C_1^-$</td>
<td></td>
<td>$-E_b + U_{LP}$</td>
</tr>
</tbody>
</table>

Fig. 14
bonding states are pushed up from the LP energy more than bonding states pushed down. Thus the next configuration shown, $C_3^o$ - a neutral three fold co-ordination atom with an extra energy than $C_2^o$ by an amount $\Delta$. The $C_3^+$ configuration, with energy of $-3E_b$, is the defect having the lowest energy. The energy of $C_3^-$ is $-E_b+2\Delta+U_{\sigma^*}$, the positive correlation energy term $U_{\sigma^*}$ arises because two electrons are in the anti-bonding state. The extra electron at a 'normal' dangling bond $C_1^o$ is indistinguishable from the two lone pair of electrons at the site and so the energy of this defect is $-E_b$. Finally, a negatively charged dangling bond, $C_1^-$, having four electrons in the lone pair state: its energy is $-E_b+U_{LP}$, the second term arising from the correlation energy in this level. The reaction, corresponding to Kastner's notation is

$$2C_2^o \rightarrow C_3^+ + C_1^-,$$

which can be seen exothermic if

$$2\Delta - U_{LP} > 0$$

The defects $C_3^+$ and $C_1^-$ have been called by Kastner a valence alternation pair (VAP). The energy required to create VAP is $U_{LP}$. The concentration of VAP's present in a sample prepared by cooling a melt, assuming equilibrium at the $T_g$, is then given by

$$N \exp \left( \frac{U_{LP}}{2kT_g} \right)$$
where \( N \) is the concentration of lattice sites.

The concentration might be expected to be lower for films deposited on to substrates at temperatures \( T < T_g \).

The energy to create VAP's may be reduced if they form close to each other because of the Coulomb energy of attraction. Such bound pairs have been called by Kastner; intimate valence alternation pairs (IVAP'S). It may be mentioned here that VAP's pin the Fermi energy, IVAP's do not. The concentration of VAP's is expected to be far more sensitive than that of the IVAP's to the addition of dopants that form charged centers. The drift mobilities, will be influenced more by VAP's since the latter are essentially neutral if the pair separation is compared to an inter-atomic spacing. Luminescence could, in principle, arise from either VAP's or IVAP's.

The various under an over co-ordinated sites can be considered as different charge state of the same defect. The removal of an electron from \( D' \) converts it to \( D^o \), removal of another electron converts to \( D^+ \). Furthermore they can be considered as true defects, rather than simply stretched or distorted bonds, since they either have a charge and no spin (\( D^+ \) and \( D' \)) or also spin and no charge (\( D^o \)). In absence of any other centers, the concentration of \( D^+ \) and \( D' \) are precisely equal and \( D^o \) centers will only be
created in low concentration by thermally activated transfer of an electron from D' to D⁺.

Another way of looking at the negative correlation energy which makes reaction

\[ 2D^0 \rightarrow D^+ + D^- \]
exothermic is as follows.

Let the addition of an electron from, say, the valence band to D⁺ cost an energy \( E_1 \) and the addition of an electron to the resulting \( D^0 \) an energy \( E_2 \).

Then we can write

\[ D^+ + e (+E_1) \rightarrow D^0 \]

\[ D^0 + e (+E_2) \rightarrow D^- \]

Thus

\[ 2D^0 \rightarrow D^+ + D^- + (E_1 - E_2), \]

If addition of second electron to \( D^+ \) costs less energy, then \( E_1 - E_2 \) is positive.
1.6 A Review on the Effect of Impurities in Chalcogenide Glasses

The question of the role of impurities in chalcogenide glasses arose immediately after the discovery of semiconducting properties of these glasses [25-27]. Initially it was found that impurities do not influence the conduction. According to Gubanob [28], the neighbours surrounding the foreign atoms due to the structure 'softness' rearrange themselves in such a way that the charge of the foreign atoms is not disclosed i.e., their local level found in crystalline state may disappear in non crystalline state.

According to Mott [17] the impurity does not influence the conduction because they may use all their valence electrons in order to form bonds with surrounding atoms or ions. As a result, the co-ordination number may be changed. In other words, all valance bonds of the impurity atom are saturated and therefore the impurity atom can either be donors or acceptors. Later on, this statement was related to the 8-N rule [29-31]. According to this rule, in covalent semiconductors, an atom which has N valence electrons (N ≥ 4) takes part in 8-N bonds, i.e., has 8-N nearest neighbour atoms. This rule is valid not only for impurity atoms but also for the host atoms of the non crystalline materials. This has been confirmed on systems Ge-Sb-Se [32], Ge-As-Se [33] prepared by quenching technique. The validity of this rule has been confirmed in experiments [34] of concerning \( \text{As}_2\text{Se}_3 \) doped with 0.25 at \% Sn. When 1 at \% of Pt, Au, Fe [33-35], and Co [36] have been introduced in glassy \( \text{As}_2\text{Se}_3 \) the maximum valance has been revealed according to the
Mossbaur effect and the impurity particularly do not influence the conductivity. The activation energy of $\text{As}_2\text{Se}_3$ does not change with doping upto 1 to 5 at % of Ge and Sn [37]. Many workers incorporated the 3d-metals (Mn, Fe, Ni, Co) [38] into $\text{As}_2\text{Se}_3$, exceeding the concentration 0.5 to 1 at %, the sample became crystalline. Low concentration does not influence the conductivity. This conclusion was experimentally confirmed by Pfister and Morgan [39].

In 1962, results were published about the electrical activity of impurities. According to Danilov [40] the double activation energy of glassy $\text{As}_2\text{Se}_3$ changes from 1.83 to 0.87 eV when the concentration of Cu was increased from 0.19 at %. This was also confirmed by some workers [41-42]. An analogous change of conductivity has been observed in glassy $\text{As}_2\text{Se}_3$ doped with Ag [43]. But these workers [40, 41, 43] have not measured the optical gap ($E_g$) and hence no conclusion can be made whether the increase of conductivity is due to the shift of Fermi level or to the decrease of $E_g$.

According to Edmond [44] an increase in $\sigma$ by a factor of 2 has been observed when the Ag concentration is 1 at %. At the same time a large increase of $\sigma$ has been observed in glassy $\text{As}_2\text{Se}_3$ doped with 1 at % Ag [44-49] and Cu [45-49]. However, the change of $\Delta E$ is equal to 0.1 eV and the increase of $\sigma$ has been explained by the lowering of the barriers when Ag is incorporated because a large growth of the pre-exponential factor is
observed. A drastic change in $\Delta E$ has been observed for $\text{As}_2\text{Se}_3$ containing As, Ga, In [50-53], and Hg [54].

Kolomiets et al. [55] have shown that $E_g$ falls by 0.04 eV only, when $x$ increases from 0.05 to 0.25 in $\text{As}_2\text{Se}_3\text{Ag}_x$. Simultaneously $\Delta E$ changes considerably ($\sim 0.18$ eV). The authors have suggested that part of Ag is incorporated in the glass is such a way that a charged impurity level is created and the Fermi level shift occurs. Later on, a large change of $\Delta E$ has been observed in the vicinity of the glass transition temperature $T_g$ (from 0.9 eV at $x = 0$ upto 0.6 eV at $x = 0.25$). Adreev et al. have measured the impurity conduction in $\text{As}_2\text{Se}_3\text{Ag}_x$ at $x = 0.06$ and 0.25 in a wide temperature range. $\ln \sigma$ as a function of $1/T$ has another slope at $T \geq T_g$, i.e., a transition from impurity conduction to intrinsic conduction has been observed. The decrease of $\Delta E$ by 0.13 eV has been observed in $\text{Te}_{48}\text{As}_{30}\text{Ge}_{30}\text{Si}_{12}$ with Mn at nearly unchanged value of $E_g$ [56-57]. Parallel measurements of $E_g$ and $\Delta E$ made for $\text{As}_2\text{Se}_3 + \text{Cu}$ [58] and $\text{As}_2\text{Se}_3+ (\text{Cu, Ag})$ [58] give an additional proof that the early information about the conductivity increase in these systems witnesses also the impurity conduction. No change in $\Delta E$ was observed in case of Cu and Fe introduced in $\text{Ge}_{15}\text{Se}_{85}$ but 1 at% In increases $\sigma$ by as much as 1.5 to 2 orders of magnitude [59].

In systems Ge - Bi - S and Ge - Bi - Se, containing 20-25 at% of Ge and less than 20 at% Bi, the electrical conductivity increases gradually with Bi content [60-62] and in the vicinity of 7-9 at% Bi it increases abruptly by
many orders [61-65], changing from p to n-type. Optical absorption measurements reveal a relatively large decrease of the optical gap $E_g$ by the incorporation of the first amount of Bi (2.5 at %). Further addition of Bi caused a very small change of $E_g$, in contrast to the drastic decrease in the activation energy for conduction between $x= 9$ and 10. Tohge et al. [63,66] have shown that the resistivity at 25 °c of $\text{Ge}_{20}\text{Bi}_x\text{Se}_{70-x}\text{Te}_{10}$ glasses is about four orders of magnitude lower for $x< 10$ compared to the corresponding $\text{Ge}_{20}\text{Bi}_x\text{S}_{80-x}$ glasses. In the Ge-Bi-Se-Te the conduction type changed from p- to n-type at practically the same value of $x$ ($\geq 9$ at % Bi). For n-type conductivity, the authors of ref [41-46] suggest that the glasses of Ge-Bi-S and Ge-Bi-Se systems are inhomogeneous and contain some microregions rich in Bi. Nagels et al. [67] investigated the incorporation of Bi into sulphur containing glasses of the type $\text{Ge}_{20}\text{S}_{80}$ and also the effect of mixed Bi-Sb doping in $\text{GeSe}_{3.5}$ glasses.

1.7 A Review of Experimental Results on Photoconductivity in Chalcogenide Glasses

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 - Fritzsche - Ovhinsky model of the band structure. Several variants of the original model have been introduced to interpret the photoconductivity data in chalcogenide glasses [68].

A contrasting approach was put forward by Main and Owen [69] who start from a band model showing discrete sets of localized states. This picture clearly resembles the one, which is commonly used in the crystalline state. When measured as a function of temperature, the photoconductivity of most amorphous semiconductors shows a typical behaviour [70].

Main and Owen [69] measured the steady-state photocurrent of amorphous As$_2$Te$_3$ (a) as a function of the photon flux at two different temperatures and (b) as a function of temperature. A striking feature is that there are well-defined activation energies involved in the temperature dependence of photoconductivity. This behavior suggests that the recombination centers are located at relatively discrete levels of localized states. Main and Owen have interpreted their data based on a simple four level model containing an electron trap and a hole trap.

The photoconductivity kinetics of amorphous and vitreous semiconductors is characterized by fast and slow components of photoresponse [71-77]. The time constant of the fast component is $\tau_p = 10^{-4}$ to $10^{-3}$ sec. The slow components have time constant in the order of seconds and
tens of seconds. The contribution of both components to the general process of establishing stationary current values depends on the composition, intensity, temperature, etc.

With growing excitation intensity, the amplitude of the fast photoresponse component rises abruptly, while the amplitude of the slow components is quickly saturated. This situation is typical for most materials investigated. The inertia of photo-response decreases with rising temperature and at additional constant illumination of the specimens.

In [75] an abrupt change of the relationship between fast and slow components of photoconductivity with the composition variation of the Se-As vitreous system has been discovered. With growing As content the amplitude of the slow component decreases, reach a minimum at the composition Se$_{90}$As$_{10}$, and with further increase of As content grows again.

In vitreous Tl$_2$SeAs$_2$, the appearance of essentially slow components of photoconductivity has been discovered at low temperatures. After illumination the conductivity of the specimen increases by two orders of magnitude and remains high for a few hours [78].

The complex character of the photoresponse kinetics has been detected in vitreous semiconductors of the system Se-As-Tl [79]. The photoconductivity in vitreous samples of As$_2$S$_3$ was established [80-83] to
have a strong influence of the wavelength of the exciting light on photoresponse kinetics. It has been demonstrated [83-85] that when the specimen are irradiated by short wavelength \((\lambda < 0.65 \mu m)\) of great intensity, the slow components are absent from photo-response kinetics. Meanwhile, irradiation by light with wavelengths \((\lambda \geq 0.75 \mu m)\) results in slow photo-response and the time constant of the photo-response and the time constant of the photocurrent growth and decay increases continuously with increasing wavelengths. In [84], the specific features of the energy spectrum of vitreous semiconductors are taken into account. The short-wavelength excitation is connected with the direct appearance of delocalized photo holes, while the long -wavelength excitation is associated with the generation of localized photoholes and with their subsequent additional thermal excitation which requires a certain time. Transient photoconductivity measurements have also been studied by many other workers [85-88].

Transient photoconductivity measurements have been made in vacuum evaporated thin films of Ge\(_{22}\)Se\(_{78}\) by Goel et. al. [89]. It has been observed that, under certain experimental conditions, the rise of photoconductivity shows an anomalous behaviour before attaining the steady state. Transient photoconductivity measurements have been made in vacuum evaporated thin films of Se\(_{80}\)Te\(_{20}\) by Tripathi et. al. [90]. They have also
observed anomalous behaviour in the rise of photoconductivity similar to the case mentioned above.

Long-term photoconductivity decays have been investigated in glassy samples of As$_2$Se$_3$ containing silver or copper up to 1.5 % by Satoh et. al. [91]. A pronounced decrease in photoconductivity is observed with the addition of impurities up to 0.1 %. Photoconductivity decay characteristics for all the samples examined are well represented by the extended exponential curve, which can be derived under the assumption of dispersive transport. Activation energy of transient photoconductivity decreases with the addition of silver and copper. Recombination rate increases with the impurity content in a low concentration range. Recombination centers are considered to be created by the addition of impurities. In case of copper, the recombination rate tends to decrease in the concentration range above 0.1 at%.

The effect of photo-crystallization on the transient photoconductivity in amorphous Se$_{80}$Te$_{20}$ has been studied by Dixit et. al. [92]. It is observed that the decay of photoconductivity becomes slower on crystallization. Similar conclusions have also been drawn in case of amorphous Se$_{65}$Te$_{20}$Sb$_{15}$. The results have been explained in terms of increased defect states on crystallization.
Tonchev et.al. [93] have studied the effect of Sb incorporation on the photoconductivity in amorphous Se and found that photoconducting properties are highly composition dependent. The effect of Sn doping on photoconductivity in a-As$_2$Se$_3$ films have been studied by Iovu et.al. [94] and found that the shape of photocurrent transients are mainly controlled by deep carrier trapping. The effect of photoinduced anisotrophy of photoconductivity in chalcogenide amorphous films of As-Se, Sb-S and Ge-Pb-S has been studied by Lyubin et al [95]. The effect of In incorporation in amorphous Se-Ge system has been studied by Singh et.al [96] and found that the photoconductive decay is non-exponential in these materials.

It is clear from the above experimental results that the incorporation of third element in binary chalcogenide glassy systems does affect the photoconducting properties drastically and hence more and more studies are required to find out more and more photosensitive glasses suitable for many solid state device applications.

1.8 Selection of the Problem

As discussed in section 1.4 the most accepted models in amorphous semiconductors consider a band gap due to short-range order present in these semiconductors. Experimentally also it is not contradictory as one observes optical absorption edge in these materials. Since the absorption edge in these materials is not sharp and has a tailing, the models consider the tailing at the
band edges due to localized states which is expected due to the absence of long range order in these materials.

In addition to localized states near band edges, the band model considers the localized states in the energy gap near Fermi level. Such localized states are assigned to the structural defects, which may be created during preparation of these materials.

The number and energy distribution of these defect states is found to be different in different materials. In fact, this has been a major problem with glassy semiconductors, which have restricted the application of these materials in many devices where such defect states act as a trap and degrade the quality of the device. Efforts are on to obtain materials which have small number of defects so that their electrical properties could be made as good as in case crystalline semiconductors.

The defect states present in the mobility gap controls many electrical and optical properties of these materials. The present thesis is an attempt to study defect controlled electrical properties.

DC conductivity in chalcogenide glasses is affected by the presence of localized states at the band edges as well as the defect states present in the mobility gap. The present author has therefore studied the behavior of DC conductivity in some important glassy semiconductors.

Photoconductivity is also affected by the presence of defect states in the mobility gap as they act as recombination centers or as traps depending
upon the position of the Fermi level. As the kinetics of photoconductivity depends strongly on the recombination mechanism and trapping effects, such studies give an idea of the distribution of defect states in these materials. In this sense, photoconductivity is a defect controlled property and hence need more thorough investigations to find out better and better photosensitive materials in glassy state.

The photoconducting property of these materials are important from application point of view also as these materials can be used for light dependent resistance, photovoltaic cell and xeroxing applications.

Some of the glassy alloys (Se–Te and Se - In) are found to be more suitable for xeroxing and photovoltaic application as compared to pure selenium due to their better photosensitivity. Therefore, the photoconductivity studies of these materials are important from application point of view.

The efficiency of various semiconductor devices, e.g., solar cells, junction diodes, light emitting diodes is also affected by the presence of the traps in semiconductor materials. These traps in general degrade the quality of the device and make them unsuitable for long-term uses. Therefore, the nature of traps and their parameters (trap density, their effectiveness for capturing carriers) are very important to study.

Apart from the photoconductivity measurements, thermally stimulated currents technique (popularly known as TSC) is also used for this purpose.
In TSC, the sample is illuminated at low temperatures with light of proper energy so that excess carriers are generated and fill the traps which remains filled even if the illumination is put off. Now if the sample is heated at a constant rate, the excess carriers in the traps are released and can be collected by a small electric field resulting in excess current known as TSC. This current signal has various information about the traps in the material.

The aim of the present work is to study d.c. conductivity, photoconductivity and thermally stimulated currents in chalcogenide glasses. All these measurements depend strongly on the concentration and their energy distribution.

The d.c. conductivity studies have been made as a function of temperature and the activation energy for d.c. conduction and pre-exponential factor are determined from these measurements. A correlation is observed between the activation energy and the pre exponential factor. For the detailed analysis of this correlation a study has been made by changing activation energy in different ways. One method of changing the activation energy is by changing the composition of the glassy system i.e., by changing the percentage of the constituent elements in a chosen glassy system. We have also changed activation energy by shifting Fermi level of a chosen glassy alloy by shining light of different intensities and also by applying different electric fields where high field conduction effects are predominant.
Photoconductivity measurements are made as a function of temperature and intensity of light. The measurements of rise and decay of photoconductivity has also been made at different temperatures and from the decay kinetics, some useful informations have been obtained which are useful in understanding the electronic structure in these materials.

The thermally stimulated currents have also been studied where a maximum is observed at a particular temperature. From the heating rate dependence of this maximum value, the position of the traps has been determined from this experiment.

For all the above studies, the present author has selected two important glassy systems Se-In and Se-Te. In case of Se-In, Pb is added as a third element, as it is reported that p to n transition takes place in this ternary alloy (Se-In-Pb) at a particular concentration of Pb. This is the first non-germanium alloy which is found to have such transitions. Earlier reports show such transitions in Ge containing chalcogenide glasses only. In case of Se-Te alloys the author has chosen Ge as third element as it has been reported that Ge addition to binary system may influence the defect states and hence influence the electrical properties of the binary Se-Te alloy drastically.

Chapter 1 of the present thesis gives an introduction to amorphous semiconductors in general and chalcogenide glasses in particular. The
selection of the problem for the present work is also given in the same chapter.

Chapter 2 of the thesis gives experimental details of sample preparation and characterization. The experimental details of sample holder used and other details of d.c. conductivity, photoconductivity and thermally stimulated current measurements have also been given in the same chapter.

Chapter 3 of the thesis reports the d.c. conductivity measurements in $\text{a-Se}_{75}\text{In}_{25-x}\text{Pb}_x$ ($x = 0, 4, 6$ and $10$) system. The chapter reports an interesting correlation between pre-exponential factor and the activation energy which has been changed by different methods. Such a systematic study in a particular alloy system has been made for the first time in case of chalcogenide glasses. A suitable explanation is also given in terms of the localized states present in these glasses.

Chapter 4 of the thesis reports the photoconductivity measurements in $\text{a-Se}_{75}\text{In}_{25-x}\text{Pb}_x$ ($x = 0, 4, 6$ and $10$). An analysis of the transient photoconductivity data is made in terms of the defect states present in this system. Composition dependence of photoconductive parameters has also been reported in this chapter.

Chapter 5 of the thesis reports the photoconductivity measurements in $\text{a-Se}_{80-x}\text{Te}_{20}\text{Ge}_x$ ($x = 0, 5, 10, 15$ and $20$) system. The photosensitivity is found to be highest for $x = 20$ and hence detailed study of photoconductivity is made for $\text{a-Se}_{60}\text{Te}_{20}\text{Ge}_{20}$. Photoconductivity rises and decays quite fast in
this system. An analysis of the photoconductivity data is made in terms of the defect states present in this system.

Chapter 6 of the thesis reports the thermally stimulated current (TSC) measurements in two samples (namely a-Se$_{60}$Te$_{20}$Ge$_{20}$ and a-Se$_{75}$In$_{25}$Pb$_4$) in two different series a-Se$_{80-x}$Te$_{20}$Ge$_x$ and a-Se$_{75}$In$_{25-x}$Pb$_x$. The selection of these two samples is made based on the highest photosensitivity observed in these samples as compared to other samples in the respective series (see chapters 4 and 5). Experimental results indicate that such a current is measurable where defect density is small and photosensitivity is large for example in case of a-Se$_{80-x}$Te$_{20}$Ge$_x$. Using the standard theory of TSC, trap depths have been calculated. These traps are caused due to defect states in the mobility gap of these materials.