CHAPTER - I

AN INTRODUCTION TO GLASSY SEMICONDUCTORS
AND THE SELECTION OF THE PROBLEM
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1.1 WHAT IS A GLASS?

Glass is a solid substance which is continuous with and analogous to 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. Obviously, unlike crystalline solids, a glass lacks long range order. However, a short range order upto a few atomic distances may be present in glassy materials.

Glass is a sub group of non-crystalline solids which can also be made in non-crystalline state by various other methods, e.g., evaporation, electrolytic deposition, gas discharge or high energy bombardment on crystals apart from the cooling from the melt. Non-crystalline solids are also termed as amorphous solids as it was found that those solids which were known as amorphous by fractography were also found non-crystalline as evidenced by X-ray or electron diffraction techniques. Another synonym for glass is vitreous which also means non-crystalline.

Glass is one of the earliest creation of the mankind. Perhaps, no other material possesses so unique combi-
nation of physical and chemical properties such as transparency, ability to withstand high temperatures, a good mechanical strength and low cost etc.

1.2 AN INTRODUCTION TO GLASSY SEMICONDUCTORS

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 counterparts 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. No experimental result was also available which showed the semiconducting behaviour of glassy substances. In 1955, however, B.T. Kolomietz and his associates in USSR first used other sixth group elements (S, Se, Te) instead of conventional element 'O' which was used to prepare glasses at that time. Unlike the conventional oxide glasses, a special name 'chalcogenide glasses' was given to semiconducting glasses. Later on, some other materials were also prepared in the glassy state which showed semiconducting properties. A
detailed classification is given in the next section.

As mentioned above, the first kind of glassy semiconductor was prepared by Kolomiets et al. They found that these glassy semiconductors behave like intrinsic crystalline semiconductors [1]. These workers 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 class of materials started after the publication of Ovshinsky's paper who reported [2] two types of switching phenomena in these glassy semiconductors. Since then, the application of these glassy semiconductors, either realized or anticipated, include a very wide spectrum such as 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, infrared lenses, ultrasonic delay lines and microfiche transparencies, in addition to the exciting applications in xerography. The high conductivity of these glasses and the absence of ionic conduction in them led scientists to study their electrical and physicochemical properties. Further, the advantage of preparing these glassy semiconductors in thin film form makes them adaptable to integration with other solid state technologies.
1.3 **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 neighbours 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.

The amorphous semiconductors can be classified according to the differences in chemical bonding. These semiconductors may be grouped into three major categories as shown below.

**Classification and Examples of Glassy Semiconductors**

1) **Covalently Bonded Amorphous Semiconductors**

A. Tetrahedral Amorphous Films

Si, Ge, SiC, InSb, GaAs, GaSb .......

B. Tetrahedral Glasses, $A^{II} B^{IV} C_{2}$

Cd Ge$_x$As$_2$, Cd Si$_x$P$_2$, Zn Si$_x$P$_2$, Cd Sn$_x$As$_2$ ......

C. Lone Pair Semiconductors

I. Elements and compounds

Se, S, Te, As$_2$Se$_3$, As$_2$S$_3$ ......

II. Cross-linked networks

Ge - Sb - Se  
Ge - As - Se  
As - Se - Te  
Se - Ge - As - Te  
As$_2$Se$_3$ - As$_2$Te$_3$  
Tl$_2$Se$_3$ - As$_2$Te$_3$
D. Others

B, As, \((\text{Cu}_{1-x} \text{Au}_x) \text{Te}_2\) ...

ii) Semiconducting Oxide Glasses

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

iii) Dielectric Films

\(\text{SiO}_x, \text{Al}_2\text{O}_3, \text{ZrO}_2, \text{Ta}_2\text{O}_3, \text{Si}_3\text{N}_4, \text{BN}, \) ...

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 [Kastner (4)] stems from the fact that their properties are primarily influenced by the two non-bonding \(p\)-orbitals of the group VI chalcogen elements in two fold co-ordination. As they contain chalcogen elements in large proportions, they are also known as chalcogenide glasses.

Among the lone pair semiconductors it is important to distinguish (i) the elements and compounds with a considerable range of local order, and (ii) the three-dimensional network structures. The first of these sub-groups contain molecular complexes of larger size which are held together...
with weak Vander waals forces. The three dimensionally cross-linked network structure is approximately more close to the ideal of structural disorder.

The second main group contains the oxide glasses, which have strong ionic bonds and are usually good insulators but which can be made semiconducting by the addition of transition metal ions in different valence 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 deviations from stoichiometry and the presence of defect centers which act as donors and acceptors. According to Jonscher [5] and Hill [6], the electronic properties of these films distinguish them from the covalent amorphous solids.

From the above discussion it is clear that glassy semiconductors form a subset of amorphous semiconductors which include only those amorphous solids which can be prepared from the melt. 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 electrical properties of chalcogenide glasses, i.e.,
the category i (C) in the classification table mentioned on page 4.

1.4 PREPARATION OF CHALCOGENIDE GLASSY SEMICONDUCTORS

Chalcogenide glasses are prepared by quenching from the melt or by condensing vapours on a substrate (thin films). This requires the prevention of the nucleation and growth processes which are responsible for crystallization. Whether or not a particular material can be cooled to form a glass depends upon the rates of the atomic/molecular transport processes which are involved in the nucleation and growth. The process of cooling introduces a progressive increase in the viscosity of the material.

It is necessary that a glass forming region of a specific composition be prepared, reacted and quenched. The extent of the glass forming region is to some extent dependent upon the quench-rate or the amount of material used in the sample preparation.

Fig (1.1) shows a typical volume temperature relationship for selenium which conveniently goes into glassy state when the melt is cooled below its freezing point ($T_{f.p.}$). It is evident from the figure that the first order thermodynamic parameter, i.e., volume, does not undergo a discontinuous change with respect to temperature. However, nature of the curve and hence the nature of the glassy state does depend upon the rate of cooling (Fig 1.1).
Fig. 1.1
1.5 CHEMICAL BOND DESCRIPTION OF CHALCOGENIDE GLASSY SEMICONDUCTORS

In covalently bonded amorphous semiconductors the coordination environment can adjust itself to satisfy the valence requirements of each atom in such a way that shallow donors or acceptors are not likely to occur in amorphous semiconductors [7]. Fig (1.2a) 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 split into bonding (\(\sigma\)) and antibonding (\(\sigma^*\)) states which form in tetrahedral semiconductors the valence and conduction band respectively. 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 (1.2b), in solid Se, these lone pair (LP) electrons form a band near the original p-state energy. The \(\sigma\) and \(\sigma^*\) band are split symmetrically with respect to this reference energy. The higher lying filled LP band is the valence band in these materials [8]. In LP semiconductors the occupied state from \(\sigma\) falls into the LP band and the acceptor some what above it.

The LP state of other Group VI elements form donors if they fall above the LP band of the host chalcogenide. The
Fig. 1.2-a

Fig. 1.2-b
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 third of the gap.

1.6 BAND MODELS FOR AMORPHOUS/GLASSY SEMICONDUCTORS

The carriers in amorphous systems are strongly affected by the randomness of atomic arrangement due to the absence of long range order. According to Mott [9], the spatial fluctuations in the potential caused by the configurational disorder in amorphous materials may lead to the formation of localized states. A band gap may however exist in amorphous semiconductors due to short range order in them. Due to localized states, the valence and conduction bands do not have sharp cut-off but have a tail above and below the normal band. The extent of
this tailing is expected to be enhanced in alloys which contain compositional disorder in addition to positional disorder.

The conduction in localized states takes place by hopping process with the help of thermal energy. At absolute zero of temperature, no conduction is expected in localized states. The mobility of charge carriers therefore changes suddenly from a finite value to zero in the band tails.

**Cohen-Fritzsche-Ovshinsky Model**

The CFO model [11] assumes that the tail states extend across the gap in a structureless distribution. This gradual decrease of the localized states destroys the sharpness of the conduction and valence band edges. As first noted by Mott [10], the character of the wave functions changes at critical energies $E_C$ and $E_V$ which separate the extended and localized states. Here the electron and hole mobilities drop sharply from a low-mobility band transport with finite mobility at $T = 0$ to a thermally activated tunneling between localized gap states which disappears at $T = 0$. These so called mobility edges [11] define a mobility gap $E_C - E_V$ which contains only localized states (see Fig 1.3a).

More recently, a similar model [12] was proposed by Spear to evaluate barrier formation and photoconductivity in amorphous Si. He suggested that, in chalcogenide glasses, the disorder is so great that tail of valence and conduction band overlap. Due to overlapping of the bands, there are states in
Fig. 1.3-a

Fig. 1.3-b

Fig. 1.3-c
the valence 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 valence band tail, which are positively charged.

**Davis-Mott Model**

Davis and Mott [13] proposed that the tails of localized states should be narrow and should extend a few tenths of an electron volt into the forbidden gap. The mobility edges for electrons and holes lie again at $E_C$ and $E_V$ as shown in Fig(1.3b). A stronger distinction is made between localized states which originate from lack of long range order and others which are due to defects in the structure. The defect states form longer tails but of insufficient density to pin the Fermi level. Moreover, the authors propose a band of compensated levels near the gap center in order to pin the Fermi level. According to Mott [14] the center band may split into two bands i.e., donor and acceptor band.

**Marshall-Owen Model**

In the model of Marshall and Owen [15], shown in Fig (1.3c), the position of the Fermi level is determined by bands of donors and acceptors in the upper and lower halves of the mobility gap, respectively. The concentration of donors and acceptors adjust themselves by self-compensation to be nearly
equal so that the Fermi level remains near the gap center. At low temperature it moves to one of the impurity bands because self compensation is not likely to be complete.

Small Polaron Model

According to Emin [16] charge carriers in some glassy semiconductors may enter a self trapped state (small polaron) as a result of the polarization of the surrounding atomic lattice. He argued that the presence of disorder tends to slow down a carrier. This slowing down may lead to a localization of the carrier and if the carrier stays in atomic site sufficiently long enough for atomic rearrangement to take place, it may induce displacements of the atoms in its immediate vicinity causing small polaron formation. Since small polaron is local in nature, the absence of long range order in glasses may be expected to have no significant influence on its motion.

1.7 DEFECTS IN CHALCOGENIDE GLASSY SEMICONDUCTORS

Experimental results indicate that Fermi level is pinned and doping is quite difficult in chalcogenide glasses. This is understood if one assumes a considerable density of defect states in the mobility gap of these materials. However, unlike other amorphous semiconductors, electron spin resonance is not observed in these glasses. The variable range hopping due to localized states near Fermi level as suggested by Mott [17] is also not observed in chalcogenide glasses under normal conditions of preparation. These materials show diamagnetic
behaviour unlike tetrahedral amorphous semiconductors which show paramagnetic behaviour.

Based on the above experimental findings, Anderson [18] proposed that, in these materials, there may be a strong tendency for electrons to be paired in bonding configurations, the coulomb repulsion between electrons at the same site being outweighed by a negative term in the energy due to electron-phonon interaction which leads to configurational changes in the local atomic structure. Since chalcogenide glasses contain a large quantity of chalcogen elements, where two fold coordination is expected, such configurational changes are quite likely. In case of tetrahedral amorphous semiconductors, e.g., a-Ge and a-Si, such structural changes are not favoured because of their rigid structure. The paired defect states are, therefore, observed only in chalcogen rich glassy alloys.

Street and Mott [18] and Mott, Davis and Street (MDS) [17] therefore chose to apply the Anderson negative $U_{\text{eff}}$ concept to specific defects.

Consider the two dangling bonds at the ends of the selenium chain (Fig(1.4a)). Transfer of an electron from one chain end to the other will lead to the creation of two charged defects $D^+$ and $D^-$. It is proposed that the reaction

$$2D^0 \rightarrow D^+ + D^- \quad (1)$$

is exothermic.
Fig. 1.4 (a)  

Fig. 1.4 (b)
On a configurational co-ordinate diagram (Fig (1.4b)), the positive correlation energy $U$ associated with the two electrons at $D^-$ in the absence of configurational changes become negative ($U_{\text{eff}}$) after lattice relaxation. The coordination number of Se atoms at $D^+$ is three and at $D^-$, it is one and at a normally bonded Se atom, 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.

According to Kastner et al. [20,21], the charged states of the defect are designated $C_1^-$ and $C_3^+$, C standing for chalcogenide and the subscript indicating the atomic coordination. $C_3^0$ is labelled as neutral center since 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 co-ordinated.

The structure and energies of several bonding configurations for a chalcogen are displayed in Fig (1.5). $C_2^0$ is the normal bonding configuration. In this configuration the antibonding states ($\sigma^*$) are empty and $-2E_b$ is the energy relative to the LP level. Antibonding states are pushed up from the LP energy more than bonding states are pushed down. Thus, the next configuration shown, $C_3^0$ has a higher energy than $C_2^0$ by an amount $\Delta$. The $C_3^+$ configuration, with an energy of $-3E_b$, is the defect having the lowest energy. The energy of $C_3^-$ is $-E_b + 2\Delta + U_{\sigma^*}$. The extra electron at a 'normal' dangling bond $C_1^0$
<table>
<thead>
<tr>
<th>Configuration</th>
<th>p-level occupation</th>
<th>Energy/configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2^\circ$</td>
<td></td>
<td>$-2E_b$</td>
</tr>
<tr>
<td>$C_3^\circ$</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>
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<tr>
<td>$C_1^\circ$</td>
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<td>$-E_b$</td>
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<tr>
<td>$C_1^-$</td>
<td></td>
<td>$-E_b + U_{LP}$</td>
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</tbody>
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Fig. 1.5
is distinguishable from the two lone pair electrons at the site and so the energy of this defect is \(-E_b\). Negatively charged dangling bond, \(C_1^-\), has four electrons in the lone-pair state, its energy is \(-E_b + U_{LP}\). The reaction corresponding to (1), in Kastner's notation, is

\[
2 \, C_3^0 \rightarrow C_3^+ + C_1^- \tag{2}
\]

which can be seen exothermic if

\[
2 \Delta - U_{LP} > 0 \tag{3}
\]

The charged defects \(C_3^+\) and \(C_1^-\) have been called by Kastner a valence alternation pair (VAP). Their creation, starting from a fully bonded network in which all atoms are in the \(C_2^0\) configuration can be described by

\[
2 \, C_2^0 \rightarrow C_3^+ + C_1^- \tag{4}
\]

which costs an energy

\[
-3 \, E_b - E_b + U_{LP} + 4 \, E_b = U_{LP} \tag{5}
\]

The concentration of VAP present in a sample prepared by cooling a melt, assuming equilibrium at the glass transition temperature \(T_g\), is then

\[
N \exp. \left( -U_{LP}/2kT_g \right)
\]

where \(N\) is the concentration of lattice sites. For films deposited on to a substrate at a temperature \(T < T_g\), the concentration might be expected to be lower.

\[
D^+ + e (+E_1) \rightarrow D^0 \tag{6}
\]

\[
D^0 + e (+E_2) \rightarrow D^- \tag{7}
\]
Thus

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

(8)

If the addition of the second electron to \( D^+ \) costs less energy than the first, then \( E_1 - E_2 \) is positive and the total reaction is exothermic.

1.8 ROLE OF IMPURITIES IN CHALCOGENIDE GLASSY SEMICONDUCTORS

What is the role of impurities in chalcogenide glasses? This question arose immediately after the discovery of semiconducting properties of the chalcogenide glasses [22 - 24]. Initially it was found that impurity does not influence the conduction. According to Gubanov [25], 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 [26] the impurity atoms do 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 valence bonds of the impurity atom are saturated and therefore the impurity atom can neither be donor nor acceptor. Later on, this statement was related to the 8-N rule [27 - 29]. According to this rule, in covalent semiconductors, an atom which has \( N \) valence electrons (\( N \geq 4 \)) 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 [30], Ge - As - Se [31] prepared by quenching technique. The validity of this rule has been confirmed in experiments [32] 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 valence has been revealed according to the Mössbaur effect and the impurities practically 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-metal (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] (see Fig (1.6)). 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 \( E_g \).
Fig. 1.6
According to Edmond [44] an increase in $\sigma$ by a factor of 2 has been observed when the Ag concentration is 1 at % $\gamma$. 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 $\Delta E$ for Ag found by Andreichin et al. [45,46] differs distinctly from the other data obtained. In [46] the value of $E_g/2 - \Delta E$ 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 in 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 $x = 0$ up to 0.6 eV at $x = 0.25$). Andreev 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 $T > T_g$, 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 $\text{As}_2\text{Se}_3$
Cu [58] and As$_2$S$_3$ + (Cu, Ag) [48] 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 Ge$_{15}$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 Eg by the incorporation of the first amount of Bi (2.5 at %). Further addition of Bi caused a very small change of Eg, 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 Ge$_{20}$Bi$_x$Se$_{70-x}$Te$_{10}$ glasses was about four orders of magnitude lower for x<10 compared to the corresponding Ge$_{20}$Bi$_x$Se$_{80}$ glasses. In the Ge - Bi - Se - Te glasses 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 con-
taining glasses of the type Ge\textsubscript{20}S\textsubscript{80} and also the effect of mixed Bi-Sb doping in Ge Se\textsubscript{3.5} glasses. It was also shown that in Ge\textsubscript{20}Bi\textsubscript{x} S\textsubscript{80-x} glasses with high Bi content \([x=11,12,15]\) n-type conduction occurs. In mixed doped glasses of composition \((\text{Ge Se}_{3.5})_{88}\text{Sb}_{12-x}\text{Bi}_x\) a transition from p-type for a Sb doped glass \((x=0)\) to n-type took place on addition of Bi at nearly equal concentrations of Sb and Bi \((x=6)\). The optical gap of the Ge\textsubscript{20}Bi\textsubscript{x} S\textsubscript{80-x} glasses decreased drastically on the incorporation of the first amount of Bi \((4 \text{ at } \% )\). Antimony analogues Ge\textsubscript{20} Sb\textsubscript{x} [Se (S)]\textsubscript{80-x} did not show such a strong dependence of the optical gap on the Sb content \([67]\).

In references\([68,69]\) the structure of \((\text{Ge Se}_{3.5})_{100-x}\text{Bi}_x\) \((x = 0-14)\) is studied. The addition of Bi does not nearly influence Ge Se\textsubscript{4} stretching vibrations.

Watanabe et al. \([70]\) studied the electrical and optical properties of \((\text{Ge S}_{0.42}\text{S}_{0.58})_{100-x}\text{X}_x\) where \(X = \text{Cu, Ag, Zn, Cd, Al, In or I}\). A small amount of Cu or Ag produces a large increase in dc conductivity with a decrease of the activation energy, and brings about a slight decrease of the optical gap and an increase of the stepness of the optical absorption edge. Zn, Cd, Al, In or I have not shown such behaviour. They explained their results assuming the decrease of a range of the localized states due to a reduction of disorder in the glassy structure. Panwar et al. \([71]\) observed a decrease in the conductivity and increase in the activation energy after
silver doping in the glassy alloy of \( \text{As}_{10}\text{Ge}_{15}\text{Te}_{75} \). The dielectric constant also decreases with the increase of Ag content in the glassy alloy \( \text{As}_{10}\text{Ge}_{15}\text{Te}_{75} \). The above facts can probably be linked with the increased disorder in the glassy alloy of \( \text{As}_{10}\text{Ge}_{15}\text{Te}_{75} \) after addition of Ag impurity.

Very interesting results were obtained while studying carrier drift in the Ge-Pb-S glasses. In a number of materials belonging to this system one has succeeded in observing bipolar transport of non-equilibrium charge carriers. Bipolar drift of charge carriers is in full accord with the data on the bipolar steady-state photoconduction in glasses of the Ge-Pb-S system [72].

From the above discussion, it is thus clear that the effect of impurities is quite different in different glassy systems. Same impurity element causes a drastic increase in conductivity in one system but reduces the conductivity in other. As mentioned earlier, Bi incorporation into Ge-Se system changes conduction type from \( p \) to \( n \) at about 9 at % of Bi. Sb and As which belong to the same group of the periodic table do not produce \( n \) type material when added to same glassy system. Because of such a diverse nature of experimental results, it is not easy to predict the effect of impurities in chalcogenide glassy semiconductors. Though Flasck et al. [73] have succeeded in changing conductivity by orders of magnitude by co-sputtering chalcogenide glass and impurity
atoms at low temperature, the method of putting impurities in the melt is being explored by various workers because of its relative ease of preparation method and reproducible results. Impurities have been incorporated by diffusion process also and it is reported [74,75] that some of the metallic atoms produce large increase in conductivity with change of conduction type, i.e., from p to n. However, it is interesting to note that not all kinds of impurity atoms have been found to produce drastic changes by co-sputtering at low temperature or by diffusion process below glass transition temperature.

From the above discussion it is clear that more and more experimental attempts have to be made to find a suitable dopant in a particular glassy system. As mentioned above, putting impurities in the melt is technically more simple and, therefore, needs further exploration. Bi doped Ge-Se system has already demonstrated the potentiality of this method of doping where n type bulk glass could be prepared by rapid cooling of the melt containing Bi impurity. p-n junctions have also been made using such an n type chalcogenide glassy semiconductor.

1.9 SELECTION OF THE PROBLEM

As mentioned in earlier sections, chalcogenide glassy semiconductors were first prepared by Kolomiets and his associates in USSR in 1950's. However, these workers did not find
these materials very interesting as doped semiconductors could not be made at that time. However, in 1968, Ovshinsky and his associates in USA gave a new direction to this field and reported various technical uses of glassy semiconductors. Since then, the electrical properties of these glasses are being studied in detail. Because of the glassy nature, these materials are very difficult to study theoretically as the mathematical simplicity of periodic potential no more exists in these materials. Experimentally also, these materials are a bit difficult as the properties depend upon the preparation conditions. New and new results come up which change the earlier well established concepts in glassy semiconductors.

The present thesis deals with the electrical properties, particularly dc conductivity and photoconductivity, in one of the important glassy chalcogenide systems. It has been recently reported that addition of Te to Se changes the properties of glassy Se drastically. Te itself is not photoconducting but when mixed with Se increases the photosensitivity of glassy Se. Amorphous Te itself has very small crystallization temperature but when added to amorphous Se increases the crystallization temperature of the amorphous Se. Similarly, the hardness increases after putting Te into Se. Ageing effects are also reduced if Te is incorporated into pure glassy Se.

From the above discussion it is clear that Se-Te alloys have some extra advantages over glassy Se particularly
if used in xerographic photoreceptors. The candidate, therefore, decided to study electrical properties of Se-Te system in detail. A particular binary glassy alloy Se$_{80}$Te$_{20}$ is chosen where the effect of third element (Ag, Cd, In and Sb) is studied at low (0.5 at %) and high (10 at %) concentration. Since the photoconductive properties are found to be different in glassy and crystalline state, the thesis reports the results in both the states.

Chalcogenide glasses in Se-Te system with and without additives are prepared by rapid cooling from the melt. After preparing glassy alloys, their amorphous thin films are prepared by vacuum evaporation technique using a standard coating unit. The details of the sample preparation are given in the next chapter.

Chapter 2 describes the details of sample preparation, and structural characterization. The experimental details for the electrical measurements have also been given in the same chapter. Chapter 3 deals with the steady state and transient photoconductivity measurements in binary Se$_{80}$Te$_{20}$ alloy in amorphous thin films. Effect of crystallization on the photoconductive properties is also discussed in the same chapter. Chapter 4 deals with the effect of third element (Ag, Cd, In and Sb) on the steady state and transient photoconductivity of Se$_{80}$Te$_{20}$ system. These measurements have also been made in
amorphous and crystallized states. The last chapter deals with the effect of some metallic impurities (Ag, Cd, In and Sb) at low concentration (0.5 at %).

The results reported in the present thesis indicate that the rise and decay of photo-current is quite different in amorphous and crystallized state (annealing above crystallization temperature) in Se-Te system. An anomalous behaviour in the rise of photocurrent is observed in Se$_{80}$Te$_{20}$ amorphous films. The thesis presents a detailed study of such an unusual behaviour which is explained in terms of non-equilibrium recombination.

A study of the effect of addition of metallic atoms (Ag, Cd, In, Sb) on the electrical properties of Se-Te system shows that such metallic elements affect the photoconductivity behaviour. In some cases, it is also observed that the behaviour of impurity atoms at low and high concentration is quite different. The results could be understood if one assumes that at low concentration of impurity, doping effects are important and at higher concentration alloy formation takes place.