Chapter 1

Chalcogenide glasses- An introduction to properties of amorphous semiconductors

1.1 Introduction

Amorphous solids are non-crystalline materials that do not possess long-range periodical order in the organization of their atoms. A solid lacking long range periodic arrangement of atoms can be prepared by quickly freezing the disorder in the liquid state into the solid state. These materials undergo the phenomenon of glass transition upon reheating. The properties of amorphous or non-crystalline solids are primarily determined by the electronic configuration and chemical bonding between the adjacent atoms, in contrast to crystalline solids in which the properties are essentially determined by the long-range periodic order of their constituent atoms. In amorphous materials, the freedom from the constraint of atomic periodicity permits a wide range of material compositions to be prepared.

Amorphous materials can be electrically insulating, semiconducting or metallic in nature. There are widespread applications of amorphous insulators in the microelectronics industry [1, 2]. Amorphous semiconductors have attracted immense interest in the field of phase change memory (PCMs) applications due to their electrical and optical properties [3–6] and are potential candidates for many commercial applications [7, 8].
1.1.1 Classification of Amorphous semiconductors

The cohesive energy between atoms is the same in crystals and amorphous materials, hence amorphous semiconductors can be classified based on their chemical bonding into two broad categories, namely the covalently bonded amorphous semiconductors and the semiconducting oxide glasses [9]. The covalent semiconductors are further classified into two major groups [10, 11] -

(i) The tetrahedrally bonded amorphous solids such as amorphous silicon (a-Si), germanium (a-Ge), etc.

(ii) The chalcogenide glasses which contain one or more chalcogen elements, (sulphur, selenium and tellurium) in a combination with elements from III, IV, or V group of the periodic table.

Among these, chalcogenide glasses have attracted attention the most for a variety of reasons such as the following:

(1) Their amorphous form can be obtained in different ways such as vapour deposited thin films or melt-quenched glasses.

(2) They are suitable for applications in many fields including fiber optics, information storage etc.

Chalcogenide glassy semiconductors have been in existence for more than about 50 years but the discovery of electrical switching phenomena in chalcogenide glasses [12] has generated a new importance to the systematic study of these materials.

This thesis reports electrical, thermal and optical investigations on thallium doped chalcogenide glassy semiconductors. The following subsections provide a brief overview of the properties and characteristics of non-crystalline materials, more specifically chalcogenide glasses.
1.2 Preparation of Amorphous Solids

Amorphous solids can be obtained either by retaining an ambient temperature at
which the disordered state can exist, or alternatively by destroying the structure of a
crystal [13]. The former procedure leads to various methods that can be used to
prepare non-crystalline materials and these are shown schematically in figure-1:

a) **Furnace cooling** - In which a melt is allowed to cool slowly by simply turning off
the furnace [figure-1(a)] or by bringing the temperature down in a programmed
manner. Typical cooling rates for furnace cooling are in the range $10^{-4}$ to $10^{-1}$ K/s and
glasses such as SiO$_2$, As$_2$S$_3$, etc., can be obtained by this method.

![Figure-1: Different methods of forming amorphous solids: (a) Furnace cooling, (b) Melt-quenching, (c) Splat quenching, (d) Condensation from the gas phase.](image)

b) **Melt-quenching** - In systems such as Se, binary and ternary glasses based on Te,
etc., a faster cooling rate is required to obtain bulk glasses. These glasses are usually
obtained by quenching the melt in ice-water or NaOH + ice-water mixture [figure-
1(b)]; the typical cooling rates for melt-quenching are in the range of $10^1$ - $10^2$ K/s.
The technique sketched in figure-1(c) is another type of melt-quenching method,
known as the ‘splat-cooling’ developed specifically for metallic glasses, in which a
liquid droplet is cooled from two sides at once.

c) **The vapor-condensation techniques** [figure-1(d)] These are used to obtain
amorphous solids in thin film form, typically 5-50µm in thickness. In vapour
deposition, the evaporated material is allowed to impinge upon the surface of a cold substrate. As the atoms condense on the surface, the amorphous structure is quenched in, if conditions are suitable to avoid the crystalline configuration. Amorphous films like Si, Ge, etc., can be formed by vapour deposition method [14].

1.3 Glass transition

Though the terminologies amorphous, disordered, vitreous, non-crystalline, etc., are commonly used for defining structurally disordered solids, the term ‘glassy’ is normally used to describe a solid obtained by cooling a liquid sufficiently rapidly (quenching) below its normal freezing temperature, bypassing crystallization. Normally, under slow cooling rate, if a melt is cooled continuously, the crystallization occurs at the freezing temperature. This melt-crystal transformation is accompanied by a discontinuity in V (T); an abrupt contraction of the volume of the crystalline solid occurs [figure-2(a)]. But at sufficiently high cooling rates, the system passes through a meta-stable super-cooled liquid state into the glassy state by involving no latent heat or volume discontinuity as in the case of formation of crystals [14] [Figure-2(a)]. But a discontinuity in the second order thermodynamic parameters such as specific heat (C_p) takes place during this transition [figure-2(b)]. In figure-2(b), a discontinuity is seen in the specific heat at the freezing point (T_f) because of the latent heat associated with the crystal↔melt transition but no such latent heat singularity accompanies the glass↔supercooled liquid transition.

The temperature at which the super cooled liquid↔glass transformation occurs is called the glass transition temperature (T_g). For many glass forming systems, the viscosity of the melt (η) attains a value close to 10^{13} poise at T_g; at this value of η, used sometimes to define the glassy state, the structural relaxation time far exceeds
Figure-2: (a) Schematic illustrations of the change in volume \((V)\) with temperature \((T)\) as the two general ways of solidifying a melt namely, slow cooling to the crystalline state and the rapid quenching to the amorphous (glassy) state.

(b) Schematic illustrations of the change in specific heat at constant pressure \((C_p)\) during crystall→melt and glass transitions for \(\text{As}_2\text{S}_3\) sample.
the experimental time-scale ($\approx 10^2$ sec) and consequently the system behaves as mechanically rigid though structurally disordered. In other words, the glassy state thus reached has an elastic modulus but lacks long range order [15]. Various models have been suggested to explain the glass transition phenomenon such as configurational entropy model [16, 17], the free volume model [18–20], the bond lattice model [21], the potential barrier model [22] etc.

Bulk glasses prepared by melt-quenching method exhibit a $T_g$ when they are reheated but amorphous materials prepared by other techniques such as vapor deposition, do not exhibit the glass transition reaction. So till date the glass transition phenomenon has remained one of the most fascinating aspects in materials science and condensed-matter physics [23].

1.4 Glass Forming Ability (GFA)

The Glass Forming Ability (GFA) of a material is a very interesting subject and depends on various factors for a particular material. Based on structural, thermodynamic and kinetic factors, several models have been formulated to interpret the origin of glass formation. Zachariasen suggested a model [24] which predicts that a substance can promptly form an extended three dimensional network missing periodicity if the coordination polyhedra in the glass and the corresponding crystal are similar and the energy content in the glass is similar to that of the crystal. In the case of chalcogenide materials, the composition and the resulting atomic structure, viscosity of the melt, speed of quenching and the frustration in multi-component melt are some of the important issues which influence the GFA [15]. The Glass Forming Ability (GFA) is known to increase with the covalency of the additive element and decrease with increasing atomic mass [25]. For example, the glass forming glass
forming ability (GFA) of elements belonging to a particular column in the periodic
table follows the following order [26, 27]. The GFA of

\[
\text{Si} > \text{Ge} > \text{Sn} > \text{Pb} \\
\text{O} > \text{S} > \text{Se} > \text{Te} \\
\text{P} > \text{As} > \text{Sb} > \text{Bi}
\]

There are also models which propose that the number of nearest neighbours
within an irregular structural network must be two, three or four only for good glass
formation [28]. Using constraint theory Phillips has attempted to explain the
composition dependence of GFA in semiconducting glasses, on the basis of
percolation in network rigidity [29]. However, there is no rule/model, which can be
used universally to predict glass forming ability in a wide variety of systems.

1.5 Structural Model of Glassy semiconductor

1.5.1 The Ideal, Continuous Random Network (CRN) model

In order to understand the physical and chemical properties, knowledge of the
structural arrangement of the atoms is an essential requirement regardless of whether
the material is amorphous or crystalline. Zachariasen [24] has given the first
significant explanation for the structure of amorphous materials.

The continuous Random Network (CRN) model is one in which it is assumed
that atoms with coordination numbers \( Z \leq 4 \) are associated by direct covalent bonds in
a linked network. The local atomic structure in non-crystalline semiconductors is not
completely random; a considerable degree of short range order is present in these
materials. The basic principles of the CRN model are as follows:
(a) All the covalent bonds of each atom are saturated i.e. the coordination of the constituent atoms satisfies the 8-N rule [30] where N represents the column in the periodic table to which the element belongs.

(b) The nearest neighbour distances (bond-lengths) are allowed to vary <1% only whereas the bond angles are allowed to be noticeably dispersed (± 10%) [14].

(c) This model does not admit any defects such as dangling (unsatisfied) bonds or over-coordinated atoms.

The structure of the glass and the crystal differ in the sense that there is a significant spread in bond-angles in the glassy network. So the structural units are allowed to rotate which leads to the absence of long range order. Based on the above idea, Zachariasen constructed the structural network of an A₂B₃ glass which is as shown in figure-3.

Figure-3 (a) A₂B₃ crystal (b) A₂B₃ glass.

1.5.2 The Random Covalent Network (RCN) and Chemically Ordered Network (CON) models

Another version of the CRN model, the Random Covalent Network (RCN) and the Chemically Ordered Network (CON) model, have been proposed to explain the local structure of amorphous semiconductors [31]. The development of short range and medium range structures with composition and its influence on various
properties is discussed in topological threshold model which is a further extension of the CRN model [32–34].

The word “Random” in Covalent Network model describes the statistical distribution of bond type. For example, let a binary alloy system be $\text{A}_{1-x}\text{B}_x$ where ‘A’ and ‘B’ are two different species and ‘x’ is a normalized concentration variable. Let ‘a’ and ‘b’ be the columns in the periodic table to which the elements A and B atoms are belong to. Assuming that this system satisfies the (8-N) rule for normal covalent bonding, the coordination of the A and B atoms, $Y_a$ and $Y_b$ are given by $Y_a = (8-a)$ and $Y_b = (8-b)$ respectively [30]. Then the distribution of bond types is determined by the local co-ordinations $Y_a$ and $Y_b$ and the fractional concentrations of A and B atoms $(1-x)$ and $x$ respectively. Neglecting the relative bond energy it includes A-A, A-B, B-B for all compositions other than $x=0$ and $x=1$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Bond counting statistics using RCN and CON models for (a) 3:2 networks \textit{(e.g. As$_2$Se$_3$)} (b) 4:2 networks \textit{(e.g. SiO$_2$)}.}
\end{figure}

On the other hand Chemically Ordered Network (CON) model places emphasis on the relative bond energies and suggests that in chalcogenide glasses, heteropolar bonds are favoured over homopolar bonds. It predicts a chemically
ordered glass composition in which only heteropolar bonds are present at the value of $X_c$ is given by

$$X_c = \frac{Y_b}{Y_a + Y_b}$$

‘A’ rich compositions ($0<X<X_c$) contain A-A and A-B bonds and ‘B’ rich compositions ($1>X>X_c$) contains A-B and B-B type bonds. The bond statistics of the two models are shown in figure-4 for (3:2) and (4: 2) alloys. The RCN and CON approaches are obviously appropriate only for covalently bonded systems and not for random close-packed structures [15].

1.5.3 Network Topological Thresholds in Glassy Chalcogenides

Upon continuously changing the composition, chalcogenide glassy systems exhibit distinct changes in their physical properties at certain specific compositions, known as the Mechanical Threshold (MT) or Rigidity Percolation Threshold (RPT) and the Chemical Threshold (CT) [35–38].

The increase of higher coordinated atoms in a glassy network containing predominantly chalcogen atoms leads to a gradual transformation of flexible (floppy) and weakly cross-linked chains to a rigid three dimensional network. When the fraction of cross-linking agents arrives at a threshold value, the rigidity percolation transition occurs and a good glass could be expected to form near this threshold value [39, 32]. In covalent network glasses, the degree of cross-linking is established by the mean coordination number $\bar{r}$.

If the total number of atoms is $N$, and there are $n_r$ atoms with a coordination $r$ ($r = 2, 3, 4$), then

$$N = \sum_{r=2}^{4} n_r$$

The mean coordination $\bar{r}$ is defined as
In covalent networks, the bond lengths and angles are considerably fixed. Small shifts from the equilibrium structure can be described by a Kirkwood or Keating potential:

\[ V = \frac{\alpha}{2} (\Delta l)^2 + \frac{\beta I}{2} (\Delta \theta)^2 \]

The mean bond length is \( l \), \( \Delta l \) is the change in the bond length and \( \Delta \theta \) is the change in the bond angle. \( \beta \) is the bond-bending force which is necessary for the constraint counting approach for stability and the bond stretching term is \( \alpha \).

The other terms in the potential are assumed to be much smaller and can be neglected.

One bond is equally shared between two atoms i.e. a single constraint is associated with each bond, so \( \frac{r}{2} \) constraints are associated with each \( r \) coordinated atom. For an atom with a nearest neighbour coordination of \( r \), between any two bonds, an angle is to be specified. For each of the remaining \( (r-2) \) bonds, two bond angle constraints have to be specified. Thus the total number of bond angle constraints on an atom will be \( [1+2(r-2)] \) or \( 2r-3 \).

The total number of constraints is therefore

\[ \sum_{r=2}^{4} n_r \left[ \frac{r}{2} + (2r - 3) \right] \]

The fraction of zero–frequency modes is given by

\[ \bar{\nu} = \frac{\sum_{r=2}^{4} r n_r}{n} = \frac{\sum_{r=2}^{4} r n_r}{\sum_{r=2}^{4} n_r} \]
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When (e.g. Se chains), i.e., one third of all the modes are floppy; the glass is floppy in nature. With the addition of higher coordination (> 2) atoms to the network as cross-links, “f” drops and goes to zero at \( \bar{r}_c = 2.4 \). In this case, a phase transition from floppy to rigid mode takes place in the glassy network i.e., the glass becomes more rigid.

Signatures of this rigidity transition (also known as stiffness transition) have been found in many different chalcogenide systems in a variety of experiments such as Raman scattering \cite{41}, vibrational density of states \cite{42}, Brillouin scattering \cite{43}, Lamb-Mossbauer factors \cite{44}, resistivity \cite{45}, etc.

The above described constraint counting is not valid when one-fold coordinated (OFC) atoms (e.g. halogens, F, Cl, Br, I) are added because the number of angular forces \((2r-3)\) becomes equal to -1 when \( r = 1 \), instead of zero. This issue has recently been addressed in a compact way by a number of authors \cite{46–48}.

If \( n_1 \) is the number of one fold coordinated atoms then the zero frequency mode needs to be corrected as

\[
f = \frac{3N - \sum_{r=2}^{4} n_r \left[ \frac{r}{2} + (2r-3) \right] - n_1}{3N} \tag{1.7}
\]

Which leads to

\[
f = 2 - \frac{5}{6} \bar{r} - \frac{n_1}{3N} \tag{1.8}
\]
It is found that the stiffness transition now takes place at a lower mean coordination \( \bar{\rho} \) which is given by

\[
\bar{\rho}_c = 2.4 - 0.4 \frac{n_1}{N}
\]

(1.9)

Here, \( \frac{n_1}{N} \) is the fraction of one fold co-ordinated atoms entering as a simple correction term. It is not surprising that the transition takes place at a lower average coordination \( \bar{\rho} \), because the OFC-atoms play no role in the network connectivity.

Recently in certain glassy systems, the stiffness transition has been found to span over a range of compositions/average coordination numbers [49]. In these systems, there is an intermediate region (IP) between the floppy and the stressed rigid phase [figure-5 (ii)], existing in the range \( \bar{\rho}_{c1} \leq \bar{\rho} \leq \bar{\rho}_{c2} \).

![Figure-5(ii): Examples of (a) under constrained (Se_n), (b) optimally constrained (GeSe4), and (c) over constrained (corner-sharing Ge(Se_{1/2})_4 glassy network.](image)

The happening of an extended rigidity transition and the presence of the intermediate phase have been experimentally validated in a variety of glasses [49, 50]. Some remarkable properties such as absence of ageing or stress, weak birefringence, etc. have been observed in the intermediate phase compositions.

### 1.5.4 Chemical threshold \( X_c \)

The chemical threshold is generally thought to be the critical composition (\( X_c \)) defined by CON model at which chemical ordering is maximized due to preferring of heteropolar bonding. The composition at which highest chemical stability occurs is
called Chemical threshold (CT) of the glassy system which corresponds to the stoichiometric glass.

In the Ge$_x$Se$_{1-x}$ glassy system for example, the CT occurs when the valence demands of divalent-Se are completely satisfied by the tetravalent-Ge.

\[ 4x_c = 2(1 - x_c) \]
\[ x_c = 0.33. \]  

The coordination number can be written as

\[ r = [xr_a + (1 - x)r_b] \]

At \( x = x_c \), \( r = 2.67. \)  

Similarly for the As$_x$Se$_{1-x}$ system CT occurs at

\( x_c = 0.40 \) and \( r = 2.40. \)

Since the glass is energetically closest to the crystalline state, the glass formation is considered to be very difficult at the CT [51, 52].

### 1.6 Energy band structure of chalcogenide glasses

Electronic properties such as DC and AC conductivity, electrical switching of chalcogenide glasses etc. depend on their electronic band structure. To understand their band structure, several models have been suggested based on the basic assumption of the local structural environment. In the crystalline solids, with perfect short-range and long-range order, the energy distribution of the density of electronic states \( N(E) \) possess sharp structure in the valence and conduction bands. In these solids, the abrupt terminations at the valence band maximum and the conduction band minimum produces a well-defined forbidden energy gap.

In an amorphous solid, the long-range order is destroyed, whereas the short-range order, i.e., the interatomic distance and the valence angle, is only slightly changed. Due to this, the overall density of energy states in non-crystalline
semiconductors is nearly similar to that in the corresponding crystal. So the concept of valence and conduction band and the band gap are equally valid for these materials but the absence of long range periodic order makes the electron energy states extended within the band gap.

Figure-6(a) shows that the electronic states for crystalline materials are distributed discontinuously at the band edges whereas in glassy semiconductors the distribution of states continues into the forbidden gap [53]. The spatial fluctuation in the potential caused by the configurational disorder in amorphous materials leads to the formation of localized states which tail above and below the normal band [54, 55]. The states are localized in the sense that an electron will not diffuse away at zero temperature to other regions. Since the localized and extended states cannot coexist at the same energy, a sharp boundary also called the mobility edge exists between the extended and localized states.

![Figure-6(a): Schematic representation of the energy band structure for (i) crystalline semiconductors and (ii) amorphous semiconductors.](image)
In glassy semiconductors, the conduction band edge $E_c$ and the valence band edge $E_v$ separate the localized state from the extended state and the energy separation between $E_c$ and $E_v$ or the band gap $E_g$, is the mobility gap [figure-6(b)].

### 1.6.1 The Cohen-Fritzsche-Ovshinsky (CFO) Model

The Cohen-Fritzsche-Ovshinsky (CFO) model assumes that the tail states which are extended across the gap destroy the sharpness of the conduction and valence band edges. This model has been specifically proposed for the multi-component chalcogenide glasses used in switching devices.

In the chalcogenide alloys, the disorder is sufficiently great that the tails of the conduction and valence bands overlap, leading to an appreciable density of states in the middle of the gap. The consequence of the band overlapping is that there are states in the valence band, ordinarily filled, that have higher energies than states in the conduction band that are ordinarily unfilled. A redistribution of the electrons must take place, forming filled states in the conduction band tail, which are negatively charged, and empty states in the valence band, which are positively charged.
This model, therefore, ensures self-compensation, and pins the Fermi level close to the middle of the gap, a feature required by the electrical properties of these materials. Though the CFO model could reasonably explain the electronic band structure of a tetrahedral amorphous semiconductor \[57\], it could not account for the high transparency of the amorphous chalcogenide below a well-defined absorption edge \[58\].

**Figure-7:** Schematic density of states diagrams for amorphous semiconductors, *(a)* The Cohen-Fritzsche-Ovshinsky model, *(b)* the Davis-Mott model showing a band of compensated levels near the middle of the gap, *(c)* modified Davis-Mott model, *(d)* the Marshal and Owen model- a "real" glass with defect states.

### 1.6.2 Davis-Mott Model

To avoid the drawbacks of the CFO model, Davis and Mott accepted that there is no broad tailing in the density of states \[59\], rather, tails are localized and extended to a few tenths of an electron-volt into the forbidden gap. According to this model, near the middle of the gap there exists a band of compensated levels originating from
the defects present in the system [figure-7(b)] and this can be split into donor and acceptor which pin the Fermi level [figure-7(c)].

Experimental evidence from luminescence, photoconductivity and drift mobility measurements, have proven the existence of various localized states in the gap, which are split off from the tail states and are located at well-defined energies in the gap. These states are associated with defect centres, the nature of which is not always known. Marshall and Owen proposed a model showing bands of donors and acceptors in the upper and lower halves of the mobility gap which makes it clear 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 [figure-7(d)] [60].

1.7 The Chemical view of Band structure

The chemical view of band structure can be well explained by taking particular examples of the tetrahedrally bonded semiconductors Ge and chalcogenides Se respectively. Figure-8 depicts the chemical bonding pictures of both these cases. Germanium atom has 32 electrons of which 28 occupy low-energy orbitals making up the first three shells of states which are tightly bound to the Ge nucleus. These are "core electrons," essentially the same in the solid as in the free atom and they do not take part in the chemical bonding. There are four outer electrons of which two occupy the 4s states and another two occupy the 4p states in the atom.

On hybridization, four equivalent highly directional $sp^3$ hybrid orbitals are constructed which are divided into the bonding ($\sigma$) and anti-bonding ($\sigma^*$) states. When they form the solid, the $\sigma$ and $\sigma^*$ molecular states extend to form the VB and
CB respectively as shown in figure-8(a). The $s \rightarrow p$ promotional energy is about 6 eV, and the net lowering of energy per atom is 4 eV.

On the other hand the chalcogen atom Se has two $s$ and four $p$ electrons in the outer shell. The $s$ electrons are chemically inert because they are tightly bound to the parent atom. Among the three $p$ orbitals, one orbital contains two paired electrons of opposite spin termed as non-bonding or lone-pair ($LP$) electrons which do not take part in bonding normally. The other two $p$-orbitals each of them filled with one electron participate in bonding; thus selenium has normally 2-fold coordination. The conduction band (CB) in Se is also built up from the antibonding $\sigma^*$ orbitals as in the tetrahedral Ge but instead of the $\sigma$ state, the non-bonding or LP-states produce a band above the original $\sigma$-state energy level and act as a valence band which is depicted in figure-8(b). Since the conduction properties of chalcogenides are determined by LP band, they are also called lone-pair semiconductors [61].

The energy levels for electron states associated with an isolated dangling bond can be explained in terms of a simple molecular orbital picture such as in a-Si, a
tetrahedral semiconducting material which has $s^2p^2$ atomic electronic configuration [15]. The atomic levels hybridize to form four $sp^3$ molecular hybrids each of which admits a bonding or antibonding orbital.

**Figure-9:**  
(a) Schematic representation of the origin of valence and conduction band states for a tetrahedrally bonded semiconductor (i) atomic s- and p-states;  (ii) $sp^3$ -hybrid states; (iii) bonding ($\sigma$) and antibonding ($\sigma^*$) states; (iv) broadening of and $\sigma$- and $\sigma^*$ states into valence band (VB) and conduction band (CB).

(b) Density of states for such a band scheme, showing the localized band-tail states. A dangling-bond band is also near mid-gap, together with the band for double occupancy higher in energy by $U$ (for a positive-$U$ system).

Solid state interactions then broaden the molecular levels into bands separated by a band gap $E_g$ as shown in figure-9. A dangling bond or non bonding orbital containing a single electron will therefore have an energy level lying at the zero energy for the $sp^3$ hybrids that is to say, near the middle of the gap. Thus, structural defects such as dangling bonds are expected to introduce electron states deep into the gap.
1.8 Defects in Glassy Semiconductors

The models such as the RCN model, the CON model, etc., proposed to understand the structural network in glassy semiconductors, consider an ideal glassy network without any defects. However, free from the constraints of periodicity, glassy solids possess a wide range of defects and the electrical, optical or in general any transport property of amorphous semiconductor is profoundly controlled by these bonding defects. Among the various types of defects present, the charged defects are the most important in chalcogenide glasses [62]. Street and Mott proposed a model first, to elucidate the nature of defects in chalcogenide glassy semiconductors [63], which is based on Anderson’s proposition [64]. Subsequently, another model was proposed by Kastner et. al., which is quite successful in interpreting most of the properties exhibited by chalcogenide glasses [65].

1.8.1 The Charged Dangling Bond Model–Street and Mott model

The charged dangling bond model emphasized by Street and Mott was originally applied to chalcogenide glasses. The essential features of this model can be understood by considering twofold coordinated amorphous Se whose structure is formed with chains as shown in figure-10(a). An unpaired electron at any chain end will act as a dangling bond denoted by $D^0$ (where the superscript indicates the charge state) which is electrically neutral relative to the bulk. Electrons residing at $D^0$ centres experience a negative $U_{eff}$ and electron pairing is energetically favourable because of atomic rearrangement. Electron-lattice coupling is strong in amorphous chalcogenides because of the low atomic coordination and results in a high degree of network flexibility, more importantly because there exist non-bonding lone-pair
electrons which can be utilized for making additional bonds which are energetically accessible since they are lying at the top of the valence band.

Figure-10: Formation of charged defects (valance alternation pairs) in chalcogenide glasses. (a) Illustration of the formation of threefold coordinated $D^+$ ($C_3^+$) and singly coordinated $D^-$ ($C_1^-$) defect centres by the exchange of an electron between two $D^0$ ($C_1^0$) centres [67].

(b) Configuration-coordinate diagram for the formation of a $D^+ - D^-$ pair. Exchange of an electron between two $D^0$ centres to give a $D^+ - D^-$ pair at the same configuration costs the Hubbard energy $U$. The $D^+ - D^-$ centres subsequently relax to a different configuration and the overall energy is lowered by the effective correlation energy $U_{\text{eff}}$.

If the two chain ends come closer to each other, transfer of an electron from one chain end to other will occur, leading to the creation of two charged defects $D^+$ and $D^-$ following the reaction – $2D^0 \rightarrow D^+ + D^-$

$$\text{(1.12)}$$

The defect $D^+$ is positively charged and $D^-$ is negatively charged. The defect $D^+$ becomes three fold coordinated because an extra bond with a neighbouring chain is formed by utilizing the nonbonding lone-pair electrons whereas $D^-$ is one fold coordinated and normally bonded Se is twofold coordinated.

The lattice distortion is therefore negligible at $D^-$, considerable at $D^+$ and intermediate at $D^0$. If the addition of an electron from the valence band to $D^+$ costs energy $E_1$ and the addition of an electron to $D^0$ costs energy $E_2$, then
\begin{align*}
D^+ + e(+E_1) &\rightarrow D^0 \\
D^0 + e(+E_2) &\rightarrow D^- \\
2D^0 &\rightarrow D^+ + D^- + (E_1 - E_2) \\
\end{align*}

The above reaction (1.13) is exothermic if $E_2 < E_1$. The same exothermic reaction can be illustrated in terms of a configurational diagram as shown in figure-10(b) \cite{66}. The appropriate configurational coordinate $q$ in this case can be taken as the sum of distances between two $D^0$ centres and their respective nearest neighbour atoms, $q_1 + q_2$. Transfer of an electron between two $D^0$ centres without change in configuration costs the Hubbard energy $U$ but the lowest energy state for the two resulting oppositely charged centres lies at a different configurational coordinate because of atomic relaxation (bonding) that takes place at the $D^+$ centres; the energy for this equilibrium configuration is lower by $U_{\text{eff}}$ than that for the two $D^0$ centres.

It can be understood from the figure-10(b) that the positive correlation energy $U$ associated with two electrons at one site is turned into an effective negative correlation energy $U_{\text{eff}}$ because of the configurational changes or in other words, the lowest energy configuration for the charged defects lies at an energy lesser than that for two centres $D^0$ by $U_{\text{eff}}$.

### 1.8.2 Kastner-Adler-Fritzsche (KAF) model

Figure-11 illustrates the structure and energies for different bonding configurations for a chalcogen atom as given by the KAF model. According to the model the native defects in chalcogenide glassy semiconductors are $C_3^+$ and $C_4^-$ known as Valence Alternation Pairs (VAPs). Here, $C$ stands for the chalcogen atom and the subscript and superscript denote the coordination and charged state of the defect sites. The neutral centre is labelled as $C_3^0$ because when an extra electron is
placed on $C_3^+$ it is shared equally among the three bonds of the atom which therefore remains threefold coordinated.

In this model, the energy of a nonbonding lone pair (LP) orbital is taken to be zero and the energy per electron of any orbital is $E_b$. The normal bonding configuration is $C_2^0$, where the antibonding ($\sigma^*$) states are empty and its energy relative to the LP level is $-2E_b$ as shown in figure-11. The antibonding states are pushed up from the LP energy level more than bonding states are pushed down thus the energy of an antibonding orbital is $E_b + \Delta$, where $\Delta > 0$. The next configuration is $C_3^0$ which is a neutral threefold coordinated atom where the LP electrons have moved

<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><img src="image" alt="Diagram" /></td>
<td>$-2E_b$</td>
</tr>
<tr>
<td>$C_3^0$</td>
<td><img src="image" alt="Diagram" /></td>
<td>$-2E_b + \Delta$</td>
</tr>
<tr>
<td>$C_3^+$</td>
<td><img src="image" alt="Diagram" /></td>
<td>$-3E_b$</td>
</tr>
<tr>
<td>$C_3^-$</td>
<td><img src="image" alt="Diagram" /></td>
<td>$-E_b + 2\Delta + U_{\sigma^*}$</td>
</tr>
<tr>
<td>$C_1^0$</td>
<td><img src="image" alt="Diagram" /></td>
<td>$-E_b$</td>
</tr>
<tr>
<td>$C_1^-$</td>
<td><img src="image" alt="Diagram" /></td>
<td>$-E_b + U_{LP}$</td>
</tr>
</tbody>
</table>

*Figure-11: Electronic structure and energies of various defect configurations in a two-fold coordinated material. The straight lines represent bond ($\sigma$ states) electrons and the dots represent the nonbonding lone-pair (LP) electrons.*
Chapter 1: An introduction to properties of Chalcogenide glasses

to the $\sigma$ and $\sigma^*$ orbitals. The removal and addition of an electron makes the possibility of $C_3^+$ and $C_3^-$ respectively. The $C_3^+$ has an energy of $-3E_b$ and is the defect having the lowest energy. Whenever an additional electron is placed on an atom, there is an increase in energy due to electronic correlation. The energy of $C_3^-$ is $-E_b + 2\Delta + U_{\sigma^*}$. The positive correlation term $U_{\sigma^*}$ is included because two electrons are in the antibonding states. The extra electron at a “normal” dangling bond $C_1^0$ is indistinguishable from the two lone pair electrons at the site and so the energy of this defect is $-E_b$. Finally a negatively charged dangling bond, $C_1^-$ has 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 $C_3^+$ and $C_1^-$ pairs suggested are similar to the $D^+$ and $D^-$ defects of the Street-Mott model. The creation of these defects, starting from a fully bonded network in which all atoms are in $C_2^0$ configuration and can be described by

$$2C_2^0 \rightarrow C_3^+ + C_1^-$$

(1.14)

which costs an energy $-3E_b - E_b + U_{LP} + 4E_b = U_{LP}$

The reaction corresponding to (1.13) in Kastner’s notation, is

$$2C_3^0 \rightarrow C_3^+ + C_1^-$$

(1.15)

which can be exothermic if,

$$-4E_b + 2\Delta > -3E_b - E_b + U_{LP} \text{ i.e. if } 2\Delta - U_{LP} > 0$$

The energy to create VAPs may be reduced if they are close to each other due to Coulomb energy of attraction. Such pairs are called Intimate Valence Alternation Pairs (IVPs). The VAPs pin the Fermi energy at mid-gap, whereas IVPs do not. Both Davis-Mott and the Kastner models are used widely to describe defects in chalcogenides.
1.9 Physical properties of Chalcogenide Glasses

Chalcogenide glasses have many interesting properties and some of the properties which are relevant to the present work have been discussed in the following sections.

1.9.1 Electrical properties

1.9.1.1 Electrical conduction in chalcogenide glasses

Electrical conduction in chalcogenide glasses is one of the most studied properties and is well understood based on the Davis and Mott model. According to this model three different types of electrical conduction are possible in chalcogenide glasses namely (i) extended state conduction (ii) conduction in band tail and (iii) conduction in localized states near Fermi level.

(i) Extended state conduction

When the temperature is high enough, the charge carriers in the extended states gain enough energy to be excited beyond the mobility gap. The conductivity in this region is given by the expression [68]

\[ \sigma = \sigma_0 \exp \left( -\frac{(E_C - E_F)}{kT} \right) \]  

The pre-exponential factor \( \sigma_0 \) is given by \( \sigma_0 = eN(E_C)kT\mu_C \) where \( N(E_C) \) is density of state at the mobility edge and \( \mu_C \) is the mobility. \( (E_C - E_F) \) is the activation energy for electrical conduction. For the extended state conduction, the carrier mobility is of the order of \( 2 \text{ cm}^{-1}\text{V}^{-1}\text{s}^{-1} \) [65].

(ii) Conduction in the band tail

Conduction can occur in the band tail due to the thermally activated hopping process, during which two charge carriers move from one localized state to another
with an exchange of energy with a phonon. The hopping conductivity at the tail state \( \sigma_{hop} \) is given by \([69]\)

\[
\sigma_{hop} = \sigma_{0, hop} \frac{kT}{\Delta E} C_1 \exp \left( -\frac{(E_A - E_F + W)}{kT} \right) \tag{1.17}
\]

Where “\( W \)” is the hopping energy:

\[
\sigma_{0, hop} = \left( \frac{1}{6} \right) \nu_{hop} e^2 R^2 N(E_C) \quad \text{and} \quad C_1 = 1 - \exp \left( -\frac{\Delta E}{kT} \right) \left( 1 + \frac{\Delta E}{kT} \right).
\]

Here \( \nu_{hop} \) is the hopping frequency, \( R \) is the distance covered and \( \Delta E = E_C - E_A \).

(iii) Conduction in the Localized state at the Fermi Energy

When Fermi energy lies in a band of localized states, charge carriers can move between the localized states near \( E_F \) via a phonon-assisted tunnelling process which is analogous to impurity conduction observed in heavily doped and highly compensated semiconductors at low temperatures. The conduction in this region is given by \([70]\)

\[
\sigma = \sigma_0 \exp \left( -\frac{W}{kT} \right) \tag{1.18}
\]

where \( \sigma_0 = \left( \frac{1}{6} \right) e^2 R^2 \nu_{ph} N(E_F) \exp(-2\alpha R) \).

Here \( -\frac{W}{kT} \) is the probability of finding a phonon with excitation energy equal to the energy difference “\( W \)” between the states. \( \nu_{ph} \) is a frequency which is in the range \( 10^{12} \text{--} 10^{13} \text{ s}^{-1} \) \([69]\). \( R \) is the jumping distance which at high temperature equals the interatomic spacing and \( \alpha \) is a quantity representing the rate of fall-off of the wave function at a site.

1.10 Negative resistance and electrical switching properties in amorphous semiconductors

Non-crystalline solids exhibit various types of non-linear electric behaviour when they are subjected to high electric fields of the order of \( 10^6 \text{ Vcm}^{-1} \) \([12]\). Under such high electric fields, insulating materials will undergo destructive breakdown,
whereas semiconductors exhibit the effect of switching and negative resistance phenomenon. The negative resistance effects can be classified into six possible types as in figure-12(a-f).

**Figure-12:** Possible types of non-Ohmic behaviour observed in materials. (a) VCNR; (b) VCNR with memory; (c) CCNR; (d) CCNR with memory; (e) threshold switching; (f) memory switching.

### 1.10.1 Voltage controlled negative resistance (VCNR)

This material exhibits VCNR starting from a low resistance and shows an Ohmic behaviour up to a critical voltage $V_t$. Above $V_t$, the material passes through a negative resistance region to reach a high resistance region. When the I-V characteristic is retraced on reducing the voltage, the material will show VCNR without memory [figure-12(a)] and with memory if the high resistance state once reached, is retained even after the reduction of the field [figure-12(b)] [71].
1.10.2 Current controlled negative resistance (CCNR)

In a sample showing CCNR, the voltage increases with current initially but at a threshold current $I_t$, corresponding to a threshold voltage $V_t$, the voltage starts decreasing with increasing current, passing through a negative resistance zone to a low resistance state. On reducing the current to zero, the characteristics may be retraced as shown in the figure-12(c) or the sample may exhibit CCNR with memory as in figure-12(d) by retaining the low resistance state [71].

1.10.3 Electrical switching

The electrical switching is one of the most commercially interesting phenomena in chalcogenide glasses. After the first discovery of electrical switching by Ovshinsky [12], investigations on such materials has gained popularity due to the potential of this property in applications such as phase change memories [72]. The electrical switching characteristics of these materials is similar to that of the CCNR materials where the glasses switch to a high conducting “ON” state from a low conducting “OFF” state at threshold voltage $V_t$. The electrical switching in glassy materials can be classified into two types - reversible (threshold switching) and irreversible (memory switching) depending on the way they react to the removal of the electric field.

1.10.3.1 Memory switching

When the applied current is increased, the voltage developed in the sample will increase initially. For a threshold current $I_{th}$ the voltage obtained is maximum. On further increasing the current above $I_{th}$, the voltage starts decreasing i.e. the sample switches from high resistance “OFF” state to low resistance “ON” state. The voltage at which the material switches from high resistance “OFF” state to low resistance “ON” state is called switching voltage or threshold voltage $V_{th}$.
Chapter 1: An introduction to properties of Chalcogenide glasses

**Figure-13 (a):** The change of voltage with applied current in the case of memory switching.

**Figure-13(b):** The I-V characteristics graph for memory switching.

While removing the current, the decrease in voltage follows the same trend of decrease in current as in figure-13(a). If the current versus voltage graph is plotted, it
can be seen that the material can retain its lower resistance “ON” state as shown in figure-13(b).

1.10.3.2 Threshold switching

In the case of threshold switching, on increasing the current, the material switches from “OFF” state to “ON” state beyond the threshold voltage $V_{th}$ as in the previous case. But on reducing the current, the voltage again starts increasing and finally comes to zero showing a reverse threshold voltage $V_{tr}$ as shown in figure-14. If the current versus voltage graph is plotted, it will nearly follow its previous path as shown in figure-14. In threshold switching device, the low resistance (ON state) is held, only if the current is kept above a holding value ($I_h$). If the current is reduced below $I_h$, the device will switch back to the high resistance OFF state, retracing its original path figure-12(e).

![Threshold switching](image)

*Figure-14: The I-V characteristics graph for threshold switching.*

(Source: Figure taken from the Ph.D. thesis of M. Anbarasu, Dept. of Instrumentation and Applied Physics, Indian Institute of science. Page no. 12)
On the other hand, in memory switching devices once it is switched, it can remain in the low resistance ON state even if the current is reduced to zero [figure-12(f)] [71].

1.11 Different switching parameters in chalcogenide glasses

Some of the important parameters which are involved in the switching process are discussed below.

(a) Switching voltage ($V_{th}$)

The voltage at which the threshold/memory materials switch to the high conducting “ON” state from the low conducting OFF state is called threshold or switching voltage ($V_{th}$) which depends on the sample thickness, electrode separation, resistivity of the material, ambient temperature, nature of excitation, etc. Therefore specification of the conditions under which ($V_{th}$) is measured is important.

(b) Switching time ($t_s$)

When the voltage drop across the sample exceeds the switching voltage ($V_{th}$), the time taken by the sample to change its high resistance state to a low resistance state is known as switching time ($t_s$). It is of the order of few nanoseconds.

(c) Delay time ($t_D$)

When the applied electric field surpasses the switching voltage ($V_{th}$), chalcogenide glasses do not change their state instantly but remain in the OFF state.

![Figure-15: The time response: $t_D$ for a threshold switch and $t_{lo}$ for a memory switch][71].
for a small period of time. The time gap between the application of switching voltage pulse and the actual initiation of switching process is called the Delay time \( t_D \) (figure-15), which is typically of the order of 10\( \mu \)sec \([71, 73]\). It decreases exponentially with the over voltage \([74]\).

(d) **Lock-on time** \( t_{lo} \)

Lock-on time is relevant to memory switching. When a memory device switches to low resistance state after the delay time \( t_D \), it is essential to keep the material in the low resistance state for a lowest period of time to set the device in the memory state. This minimum period of setting time is called Lock-on time \( t_{lo} \) (figure-15) \([73, 75–76]\). If the pulse duration is less than \( t_D + t_{lo} \), the memory switch will revert back to the high resistance state. Typically the lock-on time is found to be higher than 100 \( \mu \)sec \([74]\) and depends on the applied voltage.

(e) **Recovery time** \( t_r \)

In a threshold switch sample, after it switches once, the high resistance state is brought back by reducing the current below \( I_h \), and a definite time is required by the sample to regain its original high resistance state. This time is referred as the recovery time \( t_r \) and is typically of the order of 1 \( \mu \)sec. Within the recovery time the sample will switch for the second time by a lesser switching voltage \( V_{th} \) \([71, 75]\).

(f) **Set time**

To set the device from high resistance OFF state to low resistance ON state a small time interval is required. It is called the set time and for memory switching it is the sum of \( t_D + t_{lo} \) times.

(g) **Reset time**

This is relevant to memory switching. It is the time required to bring the device back to the initial high resistance OFF state by applying appropriate voltage/current pulse.
1.12 Electrical switching mechanisms in amorphous semiconductors

There are various propositions to explain the mechanism of threshold and memory switching in glassy chalcogenides. These are explained below briefly.

(i) Purely electronic

Adler and Peterson proposed a successful explanation for threshold switching process which is based on the field induced filling of charged defects [67, 77]. In chalcogenide glasses, there are special charge defect states (traps) \( C^+_v \) & \( C^-_v \) known as Valence Alternation Pairs (VAP). Application of sufficiently large electric field leads to the excitation of the charge carriers. These carriers will fill the charge defects states present in the glass. When all the traps are filled, the lifespan of further excited charge carriers increase suddenly to a value much larger than that needed to cross the sample thickness. The higher lifetime of the carriers increases the conductivity of the material which leads to a voltage drop and the sample switches to the ON state. This process is reversible and hence, threshold switching is also referred to as reversible switching.

(ii) Space charge mechanism

One of the most widely accepted electronic processes responsible for switching is the ‘double-injection space charge model’ suggested by Henisch et. al [78] and Lucas [79]. According to this model, both electron and holes are injected by the applied field at the electrodes. These charge carriers instantly recombine with and neutralize the positively and negatively charged traps. Thus a negative and positive space charge is created adjacent to the anode and cathode respectively. At a sufficiently strong electric field, more charges are injected so that the space charge regions spread rapidly and overlap in the central area. In the region of overlapping, the material is neutral and hence the conductivity in the centre increases. Because of
the continuously increased field, the injection of carriers increases at the electrode so electrons and holes are accelerated rapidly across the neutral region. Both effects, an increased rate at which space charge overlaps and the increased rate at which defects are filled cause a sudden increase of the conductivity of the glasses leading to the ON state characteristics.

(iii) Electro-thermal

For electrical switching both electronic and thermal effects are necessary but neither is sufficient to satisfy the switching condition, by itself. Thus for any qualitative analysis of switching behaviour, both thermal and electronic effects must be considered, and the two can develop a coupled response called ‘electro-thermal’ process. Though electronic process initiates the switching, a current channel forms in the sample due to which a temperature rise of several hundred degrees takes place along this conducting channel before current shows any substantial change [80]. As a result, a thermally induced amorphous to crystalline phase transition occurs in the conducting channel and the sample is latched to the ON state [10]. The electronic process which include the thermal effect are considered the most responsible for memory switching phenomenon. If the Joule heating caused by larger current flow after the initiation of switching is sufficient to induce the phase transition from amorphous to crystalline state in the current carrying filament, memory switching is exhibited. Otherwise, the glass will exhibit threshold behaviour. A representative cyclic process which happens after the initiation of switching has been given in figure-16.
The increase in conductivity after switching leads to an increased power dissipation in the sample. As a consequence, a rise in the temperature of the conducting filament occurs due to Joule heating. The increased temperature raises the conductivity, leads to more power dissipation and further increase in temperature, this cyclic process can finally activate the phase change and memory switching in certain chalcogenide glasses. There are several factors which decide whether a chalcogenide glass will exhibit memory or threshold type electrical switching:

**The thermal stability:** Samples which undergo easy devitrification are expected to exhibit the memory behaviour even at lower ON state currents.

**Thermal diffusivity:** The rise of temperature in the conducting filament is determined by the rate of dissipation of heat away to the bulk of the material, which in turn is decided by the thermal diffusivity of the glass. In glasses with lower thermal diffusivity, memory switching is more likely compared to those with higher thermal diffusivity

**Network topological effects:** The network connectivity and rigidity (which are determined by the coordination numbers of the elements), network topological thresholds (such as rigidity percolation and chemical threshold), etc., have been found to play a crucial role in the electrical switching behaviour of glassy chalcogenides.
1.13 Electrical SET-RESET in chalcogenide glasses for information storage: Non-volatile Random Access Memory Application

The major property of chalcogenide glass is its ability to switch fast and easily between the two states - amorphous to crystalline and vice versa in a stable manner under the application of an external energy in the form of voltage/current pulse or acute laser beams. The large difference in the electrical resistivity or the optical invariables between the two states has made them a candidate for Phase Change Memory applications. To switch between the two states an energy barrier should be overcome before any structural state can be changed. If the applied energy crosses the barrier energy, it excites the material to rearrange its bond lengths and angles slightly and rapidly through the movement of individual atoms and the material shows switching behaviour optically or electrically.

*Figure-17: The SET-RESET process in amorphous in chalcogenide glasses.*
Chapter 1: An introduction to properties of Chalcogenide glasses

The electrical/optical switching has made it possible for the chalcogenide glasses to store data electrically and optically, a phenomenon that was first discovered nearly four decades ago [65, 84]. Since then substantial research efforts were centered on understanding the fundamental properties of amorphous chalcogenide semiconductors [66, 81].

When current/voltage pulse is applied it supplies the necessary heat required for crystallization, the glass transforms from amorphous to crystalline state and a permanent storage of information is established. The SET process is normally attained by applying a pulse with less amplitude but for long duration as shown in figure-17.

The RESET process is attained by applying a higher and sharper current pulse, during which local melting and re-solidification of the conducting crystalline region formed during the SET process into the amorphous state occurs as depicted in figure-18.

![Figure-18: (a) The structural transformation during RESET pulse; (b) The temperature-time profile during RESET pulse (i) and during SET pulse (ii).](image)

The amorphous and crystalline states have very different electrical resistances (figure-19), so the recorded information can be read easily and the glass is suitable for Non-Volatile Phase Change Random Access Memory Application.

The most commonly used material for an optical/electrical memory device is the Ge-Te-Sb glass. Although Ge₅Sb₂Te₅ can be triggered in amorphous and crystalline state with laser pulses as short as 10 ns, it does not phase segregate upon
crystallization like the earlier Te-rich alloys and exhibits congruent crystallization \[82\] with no large scale atomic motion.

Phase change materials can replace the existing data with new data without any intermediate erasure step resulting in high data transfer rates which can be referred to as direct-overwrite. Thus phase change materials which can be switched locally by optical means \[83–85\], are used to encode binary information in write-once and rewritable Compact Discs (CDs) and Digital Video Discs (DVDs).

**Figure-19:** The principle of operation of a chalcogenide phase change memory indicating that the structural and resistance changes during the SET and RESET operations \[72\].

### 1.13.1 Principle of erasable Optical Storage:

The phase-change optical storage is based on the structural alteration of the material from amorphous to crystalline state and vice versa on a microscopic area of the recording layer when the material is irradiated by laser/electric pulses. The recorded information is reproduced from the difference in reflectivity due to the
difference in refractive index and extinction coefficient between the two phases as shown in figure-20.

![Figure-20](image.png)

**Figure-20:** Principle of phase-change recording and temperature profile of the recording layer for the writing and erasing process [86].

There are two possible types of phase changes—one is between amorphous and crystalline phases and another is between two different crystalline phases. Only the first one is applied in rewritable phase-change optical discs. Before recording data on the phase-change optical media, the as deposited amorphous films are transformed into the crystalline state. In the writing process, the amorphous state is achieved by heating the phase-change material with sufficient high laser power above its melting point.
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point and then rapidly quenching it to room temperature. Because the atoms of the phase-change material after melting are in a disordered state and the cooling rate of the area irradiated by laser pulses is very high, the time is not sufficient for the atoms to be arranged into the ordered crystalline structure. Thus amorphous marks are formed. In the erasing process as shown in figure-20, the crystalline phase is achieved by annealing the phase-change material at the temperature between the crystallization temperature $T_c$ and the melting point $T_m$ with a medium power laser irradiation.

**Figure-21:** Schematic representation of optical recording [86].

During the irradiation period, the atoms of the phase-change media are rearranged into an ordered structure; thus the amorphous region can be changed to the crystalline state. The alteration of phase changes is accomplished by using the irradiation of laser light with a diameter of 1 μm typically.

When a laser beam having a 1 μm diameter moves on the recording materials at a linear velocity of 10 m/s, as shown in figure-21, the irradiation time of a point is only 100 ns. Hence, the available time for the energy deposition is also within this irradiation time duration. Assuming that the laser power is 10 mW, the power density of the light spot is of the order of 10 kW/mm² [86].
Since melting of a solid is virtually instantaneous, a very short laser pulses can achieve the amorphization of material, provided that the melting temperature is exceeded upon laser illumination. Because the atoms or molecules are re-arranged during crystallization, the time duration required for crystallization process depends on the crystallization speed.

Consequently, the materials suitable for phase-change memory applications should have high thermal stability in the amorphous state as well as high crystallization speed to enable the atomic rearrangement process within the energy deposition time.

There are many factors which are very important for selecting a material suitable for Set-Reset/Write-Rewrite process such as:

1) **Cyclability.** The material needs to be transformed between the amorphous and crystalline phases many times. Usually, materials without phase separation during the reversible phase transitions have good write/rewrite cyclability.

2) **Crystallization speed.** The faster the crystallization speed, the shorter the erasing time. To achieve rapid crystallization, the materials should have: (a) large atomic mobility in the amorphous and super-cooled states and (b) short atomic diffusion distance from the atomic location in the amorphous state to the lattice sites of the crystalline state. Atomic mobility is controlled by the viscosity of the super-cooled liquid. Generally speaking, a weak bond means a low viscosity force among atoms, which increases atom mobility and crystallization speed.

3) **Melting point.** Because the material must be molten by laser/electric pulses, the melting point cannot be too high. However, if it is too low, the crystallization temperature will also be low and self-crystallization may occur resulting in the amorphous phase being unstable at room temperature.
4) **Thermal stability.** The retention of data depends on the thermal stability. High stability is needed for the long life time of data at room temperature.

5) **Optical constants.** The material must be chosen such that it has enough absorption that shifts in the visible or near-infrared region with the phase transitions. Hence, metals and insulators are eliminated which leaves only semiconductors as promising materials.

Many attempts have been made to reduce the Reset pulse amplitude/power by modifying the device structure or by doping with other elements to reduce the melting temperature and to increase the crystalline resistivity [87, 88]. GeTe based glasses have been found to have both high thermal stability of an extensively cross-linked amorphous network and fast crystallization time needed for direct over-write [89]. The signature of set-reset process and the possibility of use for Random Access Phase Change Memory application have been found in thallium doped GeTe glasses reported in this thesis work.

### 1.14 Photo-thermal Effect in chalcogenide glasses

When a sample is kept under the exposure of radiation, local heating occurs due to absorption and subsequent thermalization of the incident radiation. The magnitude of absorption and the thermalized volume fraction depend on the interaction between the absorption profile and thermal transport properties of the material under investigation. If the incident radiation is modulated harmonically or in pulse, an oscillatory or transitory heat source respectively, is generated in the sample. The oscillatory heat wave can be measured by various detection schemes as shown in figure-22(a) [90, 91]. In photo-acoustic spectroscopy, the generated heat wave is converted into a pressure wave and is measured using a microphone. In a photo-
pyroelectric set-up, the heat wave is deposited directly onto a pyroelectric film and the output is measured directly.

![Diagram of various thermal spectroscopic techniques](image)

**Figure-22 (a):** The various thermal spectroscopic techniques classified based on the detection schemes.

![Diagram of photo-thermal deflection technique](image)

**Figure-22 (b):** The working principle of photo-thermal deflection technique [92].

In the case of photo-thermal deflection methods, which has been used in this work, a modulated laser beam as in figure-22(b) (shown in green) strikes the sample surface,
generates a thermal wave field, which, in turn, causes a refractive index gradient to appear in a surrounding medium. A probe laser beam travelling parallel to the surface (pink) will be deflected harmonically, due to the mirage effect. The deflection in the probe beam is detected using a position sensitive detector and the thermal parameters such as thermal diffusivity can be estimated from the deflection.

### 1.15 Thermal Diffusivity

Thermal diffusivity ($\alpha$) is one of the most important thermal transport parameters of materials which can be measured using the thermal wave technique described above. The thermal diffusivity is defined as $\alpha = \frac{k}{\rho C}$, where $k$ is the thermal conductivity, $\rho$ is the mass density and $C$ is the specific heat. Thermal diffusivity is highly sensitive to the structure of solids. In fact, thermal conductivity in non-metals is connected to the vibrations of the atoms in the network around their equilibrium positions and structural changes are expected to influence the heat diffusion process. Thermal diffusivity decides the rate at which heat can be dissipated away from the conducting crystalline channel. It has been recently pointed out that there is a strong correlation between the thermal diffusivity and the switching behaviour of chalcogenide glasses. Glasses with low thermal diffusivity are likely to exhibit memory switching and those with higher values of thermal diffusivity show threshold type switching [93] hence, the measurement of thermal diffusivity of switching glasses is important for identifying suitable materials for memory switching and, hence, non-volatile memory.
1.16 Objectives and Scope of the Present Work

The present thesis work essentially deals with studies on electrical, thermal and optical properties of Ge-Te-Tl chalcogenide glasses and elaborated investigations on their suitability for phase change memory applications.

In this work, electrical switching and thermal and optical studies have been undertaken on Ge-Te-Tl glasses over a wide range of compositions. Studies have been carried out on the I-V characteristics of these samples to understand the nature and composition dependence of their electrical switching behaviour. Electrical set-reset investigations have also been carried out to select the suitable glass for Phase Change Memory Applications. The thermal analysis on these samples has been used to obtain glass transition and crystallization temperatures, specific heat capacity, relaxation enthalpy, glass forming ability, etc. and to correlate these thermal parameters with the switching characteristics. Optical induced thermal investigations have been carried out to find out the relation with electrical properties. Further, the compositional dependence of thermal and electrical parameters of these glasses have been investigated to find out whether any intermediate phase is present or not.

The whole thesis work can be represented in graphical form as shown in chart-1.
Chapter 1: An introduction to properties of Chalcogenide glasses

Chart-1: The graphical representation of this thesis work.
Chapter 1: An introduction to properties of Chalcogenide glasses

References


Chapter 1: An introduction to properties of Chalcogenide glasses


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