1.1. Introduction

Amorphous solids, also known as non-crystalline solids do not possess long range periodic order in their constituent atoms. There is no translational periodicity in the arrangement of atoms. Though amorphous materials lack a long range order (LRO) found in the crystals they preserve a high degree of short range order (SRO) [1]. An amorphous material can be obtained by quickly arresting the disorder in the liquid state into the solid state [2]. Glasses are distinctive class of amorphous solids which exhibit the phenomenon of glass transition upon heating [3].

The properties of amorphous or non-crystalline solids are primarily determined by the electronic configuration and the nature of the chemical bonding between the adjacent atoms, in contrast to crystalline solids in which the properties are essentially determined by the LRO in their atomic arrangement. Consequently, the amorphous materials can be electrically insulating, semiconducting or conducting. Many amorphous substances are found to exhibit significant electrical conduction referred to as amorphous semiconductors. Electrical conduction is associated with electrons rather than ions in the solid, because the contribution of ions to the conductivity is usually very small. The discovery of the semiconducting properties of amorphous materials by Kolomiets and Goryunova [4, 5] has opened an exciting field of research, namely the amorphous
semiconductors. Amorphous semiconductors have attracted utmost interest, because of their potential commercial applications due to their fascinating properties [6].

This thesis deals with the thermal and electrical studies on certain metal doped Ge-Se chalcogenide glassy semiconductors. The following subsections provide an introduction to the properties of amorphous semiconductors, more specifically chalcogenide glasses.

This chapter deals with the basic properties of amorphous semiconductors namely, the basic classification, electronic band structure, preparation, structural and essential properties of chalcogenide glasses, etc.

1.2. Classification of Amorphous Semiconductors (a-SC)

Amorphous semiconductors are generally classified on the basis of the type of chemical bonding that is primarily responsible for cohesive energy of the material [7]. Based on the nature of the chemical bonding, amorphous semiconductors are generally classified into two broad groups:

(i) Ionic bonded amorphous semiconductors such as halide and oxide glasses, particularly the transition metal oxide glasses. Being ionic, the compositional variation of these materials over wide range is not possible and the pure materials have just positional disorder.

(ii) Covalently bonded amorphous semiconductors. These covalent amorphous semiconductors can be further divided into two major types [8].

(a) The tetrahedrally bonded amorphous solids such as amorphous silicon, germanium and related alloys. These materials find many applications in thin film transistors, image scanners, solar cells, optical recording and gas sensors, etc [9, 10].

(b) Chalcogenide glasses, which contain a considerable proportion of one or more of the ‘chalcogens’ (sulphur, selenium and tellurium) in a combination with elements from III, IV or V group of the periodic table. They find numerous applications in infrared optics, xerography, Phase change memories (PCM), fiber optics, X-ray imaging plates, etc. [11].
1.3. Atomic Structure of Amorphous Semiconductors

Knowledge of the structural arrangement of atoms in amorphous semiconductors is a primary prerequisite to a detailed understanding of other essential physical or chemical properties. The structural order in amorphous semiconductors can be classified into 'microscopic' and 'macroscopic' structure depending upon the length scales [12, 13].

1.3.1. Microscopic Structure

Microscopic structure of amorphous semiconductors involves the deposition of individual atoms or groups of atoms at a local level. Further this can be divided into two types namely “Short Range Order” (of the order of few Å°) and Medium Range Order” (of the order of 5-20 Å°) [14].

1.3.1.1. Short Range Order (SRO)

SRO is the smallest structural order, which is associated with a length scale of 2-5 Å° [12]. In covalently bonded amorphous semiconductors with strongly directed bonding, such as chalcogenide glasses, SRO can be defined in terms of well defined coordination polyhedra. Thus the parameters which are sufficient to describe topological SRO are the type and number Nj of nearest neighbor bond length rij, the bond angle θijk subtended at the origin atom of type ‘i’ by two neighboring atoms j and k. The neighboring atoms j and k may or may not be of same kind.

1.3.1.2. Medium Range Order (MRO)

The MRO or equivalently intermediate range order in amorphous semiconductors is the next higher level of structural organization beyond SRO extending over a length scale of 5-20 Å° [12, 14]. The MRO in covalently bonded amorphous semiconductors can be further, classified into three categories, on the basis of increasing length scales: short-range MRO (SRMRO) (length scale 3-5 Å°), intermediate MRO (IRMRO) (5-10 Å°) and long-range MRO (LRMRO) (greater than 10 Å° -20 Å°). SRMRO is
concerned with the type of connection between, and relative orientation of pairs of the coordinate polyhedra which form the basic structural units in the SRO. A structural parameter which is a measure of such orientational correlations for covalent systems with well defined bonds is the dihedral angle (\(\phi\)). The dihedral angle (\(\phi\)) is defined as the angle of rotation about a common bond required to bring into coincidence the projections, onto the plane perpendicular to this bond, of the two bonds either side of the common bond forming parts of the two connected (polyhedral) units [14]. IRMRO is associated with the phase relationships between pairs of dihedral angles for neighboring bonds. Thus, aggregates of basic polyhedra connected together to form regular rings, or clusters of atoms, lead to the occurrence of “superstructural units”.

The LRMRO is associated with the local dimensionality of a covalently bonded amorphous network; this can be ascertained by finding the dimension traced out locally over distances \(\approx 10 \, \AA\) by bond percolation among the covalent bonds of the structure, neglecting the much weaker Van der Waals bonds [15].

### 1.3.2. Macroscopic Structure

In the preceding section, the SRO and MRO in amorphous semiconductors have been discussed, with an assumption that the structure to be homogeneous in the microscopic level. However, many amorphous semiconductors are found to exhibit inhomogeneities on the macroscopic level (\(\approx 1 \mu m\)), such as voids in the vapour-deposited thin films or phase separation for certain compositions of multicomponent melt-quenched glasses. These inhomogeneities can be detected by High Resolution Electron Microscopy (HREM), optical microscopy and small angle (X-ray or neutron) scattering experiments [14].

### 1.4. Energy Band Structure of Amorphous Semiconductors

The knowledge of energy band structure is needed to understand the electrical properties of amorphous semiconductors. In crystalline semiconductors, the density of states possesses van Hove singularities and abrupt terminations at the valence band
Chapter 1: Amorphous Semiconductors and Their properties

maximum and conduction band minimum. The sharp edges in the density of states lead to a well-defined forbidden energy gap. Within the band, the states are extended, which means that the wave functions occupy the entire volume. These characteristic features are the consequences of the short range and long range orders present in the crystalline materials. In amorphous semiconductors, though the long range order is absent, a high degree of short range order is exhibited. The local structural environments in crystalline and amorphous semiconductors are found to be nearly the same. Hence, the distribution of density of energy states is similar in crystalline and amorphous semiconductors. The effect of disorder is to introduce band tailing by removing van Hove singularities [16-18]. One of the effects of disorder on the “density of states” (DOS) is to smoothen out (removal of van Hove singularities) the sharp structures in density distribution of states and the order is to cause tailing of states into the gap. An even more important consequence of disorder is that the electron states become ‘localized’ which means that the electron present in such state would be spatially confined to the vicinity of predominately a single atomic site. Further, presence of such localized sates corresponding to tail states is a consequence of the disorder.

On the basis of Anderson’s theory of localization [19], Mott [20-25] proposed that impurities had no effect in a glass since all the valence requirements can be satisfied. The disorder introduces ‘tails’ of localized states at the band edges E_c & E_v, which trail-off into the forbidden gap region (figure 1.2(a)). Further, Mott [20-25] suggested that the spatial fluctuations in the potentials, caused by the configurational disorder in amorphous materials, lead to the formation of localized tail states above and below the normal bands. Since the localized and extended sates cannot co-exist at the same energy, there is a sharp boundary (called mobility edge) between the extended and localized sates. An excursion across the mobility edges causes the carrier mobility to change by a factor of 100. All the models of the band structure of amorphous semiconductors use the concept of localized states in band tails and mobility edges. The models are proposed primarily to explain the following characteristic features, which are common to most of the amorphous semiconducting films & glasses.
1. Insensitivity of electrical conductivity of a-SC to the addition of chemical impurities, Mott explained this as due to the satisfaction of normal valance requirement of the impurity atoms in an amorphous network (8-N) rule [26].

2. Pinning of the Fermi level $E_F$ near midgap, which suggest that a high density of defect states must be present in the mobility gap [27].

3. A general similarity of the overall distribution of the density of states in the valence and conduction bands to that in the corresponding crystalline phase.

Various models, proposed to explain the electrical properties of amorphous semiconductors, are briefly discussed in the following section.

1.4.1. Physical approach

1.4.1.1. The Cohen-Fritzsche-Ovshinsky (CFO) Model

To explain some of the properties of the a-sc, in which disorder becomes extensive, Cohen, Fritzche, and Ovshinsky (CFO), proposed the model shown in figure 1.1. The CFO model [28] assumes extensive tailing of band edges as a result of both compositional and topological disorders. The conduction and valence bands extend so far into the gap that they actually overlap each other, leaving an appreciable density of states in the middle of the gap. As a result, redistribution of charges takes place, with electrons transferring from the higher region of the Valence Band (VB) tail into the lower region of the Conduction Band (CB) tail. Since the states involved are localized, this results in the formation of negatively charged filled states in the conduction band, and positively charged empty states in the valence band as shown in figure 1.2.(b) As a consequence, ensures self-compensation and pinning of the Fermi level near midgap due to overlapping tails.
Chapter 1: Amorphous Semiconductors and Their properties

Figure 1.1. The CFO model. Positive and negative signs indicate ionization of impurities due to overlap of bands [29].

Figure 1.2. Various band models of a-SC: (a) the Mott model (b) the CFO model and (c) the Davis–Mott Model (also known as Marshall and Owen model).

1.4.1.2. The Davis–Mott (DM) Model

According to Davis and Mott [30, 31], the effect of disorder is to ‘tail’ the band edges and band tails are rather narrow and extend only a few tenths of an electron volt in to the forbidden gap. Further, this model proposed the existence of a band of compensated levels near the middle of the gap originating from the defects in the random networks. In addition, they suggested that the central band splits in to donor and acceptor bands, which in-turn pin the Fermi level ($E_F$) as shown in figure 1.2(c).
Marshall and Owen in 1971 independently proposed the concept of having donor and acceptor like bands in the upper and lower halves of the mobility gap respectively [32] (figure 1.2(c)). Further, they suggested that these bands adjust themselves by a self-compensation mechanism and keep their concentrations equal, thereby fixing the $E_F$ near mid-gap.

1.4.2. Chemical approach

Origin of band gap in amorphous semiconductors can also be understood by adopting a chemical approach [33-35]. This approach depends on the short range order (SRO) and is equally applicable to both crystalline and amorphous materials. The nature of the density of states (DOS) in a solid is mainly dependent on the nature of chemical bonds, the coordination numbers of the atoms and their valence states [36].

This model can be understood by considering specific examples of germanium (Ge) and selenium (Se) which are prototypical of the two main classes of semiconductors i.e., the tetrahedrally bonded semiconductors and chalcogenide semiconductors. The four-fold coordinated Ge has highly directional $sp^3$ hybridized orbitals, which are split into the bonding ($\sigma$) and anti-bonding ($\sigma^*$) states as show in figure 1.3.

![Figure 1.3. Bonding in (a) Ge and (b) Se [33].](image-url)
The chalcogen ‘Se’ atom contains two s and four p electrons in its outermost shell. Only two of the three p states can be utilized for bonding (figure 1.3). This leaves one p-state occupied by two paired electrons of opposite spin, known as non-bonding electron pair or lone-pair (LP) electrons. These non-bonding electrons do not participate in the bonding and the bonding is actually due to the remaining two p-states (orbitals) each occupied by single electron. Thus, selenium is normally found in 2-fold coordination. Similar to Ge, the CB in Se also originates from the $\sigma^*$ states, but the highest occupied VB is formed from non-bonding states instead of the $\sigma$ states as shown in figure 1.3. Thus, unshared or non-bonding electrons (LP) states form a band near the original p-state energy and acts as the valence band [33, 37]. Since the non-bonding electrons constituting the highest VB or LP band determines the conduction properties of chalcogenides, such materials are also called lone-pair semiconductors [33].

1.5. Defects in Amorphous semiconductors

Many properties of amorphous semiconductors are controlled by the intrinsic defects, which exist in the gap states. Among these are magnetic properties, opto-electronic behavior, vibrational properties and mechanical characteristics etc. In majority of the cases, behavior resulting from the presence of defects can completely dominate that due to the intrinsic material. This is due to the low creation energy of these defects and hence they can be present in concentrations sufficiently large enough to control the transport behavior [30]. Although amorphous semiconductors are free from the constraints of periodicity, they possess a wide range of defects. Among the various types of defects present, the charged defects are the most important in the amorphous semiconductors [38]. There are two important models, proposed to explain the defect formation & its nature in amorphous semiconductors.

1.5.1. Street & Mott Model

This model was proposed by Street & Mott to elucidate the nature of defects in amorphous semiconductors [39]. This model assumes that the localized gap states are constituted by dangling bonds having concentration of $10^{18}$-10$^{19}$ cm$^{-3}$. Creating a doubly
occupied state out of the gap states, which originate from a dangling bond, is in effect creating a charged dangling bond. These charged dangling bonds have their counterparts in positively charged states, which are empty (donor) orbitals. According to this model, there are two equivalent descriptions of the formation of these charged defects. Street & Mott in 1975 designated these defects as $D^0$ (neutral dangling bond), $D^+$ and $D^-$ which are positively and negatively charged centers respectively. Where $D$ indicates that they are defects in an amorphous lattice. Based on the Anderson’s proposition [40], Street & Mott suggested that formation of $D^+$ and $D^-$ (charged pairs) from $2D^0$ states can be energetically favourable, because the coulombic interactions arising from the charged pair can give rise to local relaxations, which can decrease the positive Hubbard energy $U$ into an effective negative Hubbard energy $U$ as shown in figure 1.4.

$$2D^0 \rightarrow D^+ + D^- \quad (1.1)$$
The transformation of two neutrally charged chain-end dangling bonds ($D^0$) into charged defect sites is depicted in figure 1.5. The above reaction is considered exothermic because of the effective negative correlation energy.

This model succeeded in explaining many experimental results. However, it failed to explain the assumption of high density of dangling bonds and as a consequence, the origin of negative effective energy $U$ [42]. Further, it could not explain why a large negative effective energy $U$ characterizes the chalcogenide glasses and not the tetrahedrally bonded amorphous semiconductors [43].

Figure 1.5. Schematic representation of the process of formation of charged coordination defects from two neutral dangling bonds ((a) $\rightarrow$ (b)) in a-Se [39].

1.5.2. Kastner-Adler-Fritzche Model (KAF)

This KAF model [44] also known as Valence-Alternation model considered the process of spin pairing at defects in amorphous materials referring to it as “Valence Alternation”, introduced useful notation of the type: $\text{Chalcogen}_{\text{charge state}}^{\text{coordination}}$. For example $C_x^0$ symbolizes a doubly coordinated, neutral chalcogen atom. This model emphasizes that, the behavior of charged defects and the dominant contribution to the negative correlation energy is chemical in origin. Further, this model suggests that specific interactions
between the non-bonding orbitals give rise to unusual bonding configurations called Valence Alternation Pairs (VAP's), whose formation requires relatively small energy.

The structure and creation energies of several simple bonding configurations for chalcogens as per the KAF model are schematically shown in figure 1.6. In figure 1.6, the non-bonding (LP) energy is taken as zero, giving the bonding (σ) orbital an energy \(-E_b\) and the antibonding (σ*) orbital with an energy \(+E_b+\Delta\), where \(\Delta\) is the excess energy of the anti bonding orbital compared to the bonding orbital. Here, \(C_3^C\) is the normally bonded chalcogen atom, with an energy of \(-2E_b\). The lowest energy bonding configuration neutral defect is the three-fold coordinated atom \(C_3^C\), where the LP electrons have moved to the bonding (σ) and antibonding (σ*) orbitals. The three fold coordinated \((C_3^C)\) and the singly coordinated \((C_3^S)\) chalcogen atoms are found to possess energies of \(-2E_b + \Delta\) and \(-E_b\) respectively. Although \(C_3^S\) is a lower energy configuration, it is unstable and transforms in to \(C_3^+\) and \(C_3^-\):

\[
2C_3^0 \rightarrow C_3^+ + C_3^-
\]  

(1.2)

This reaction will cost positive correlation energy of \(U_{\sigma^+}\) because, the formation of it requires an additional correlation energy \(U_{\sigma^*}\) since two electrons must exist in the σ* state. Hence \(C_3^-\) will get transformed into \(C_3^C\) by converting the existing \(C_3^S\) into a \(C_1^-\) center:

\[
C_3^- + C_2^0 \rightarrow C_2^0 + C_1^-
\]  

(1.3)

The system can thus lower its energy by transferring two σ & σ* electrons into the LP states of one of the singly coordinated and two fold coordinated chalcogens, leading to the following reaction

\[
2C_2^0 \rightarrow C_3^+ + C_1^-
\]  

(1.4)

The net reaction is formation of a pair of coulombically charged defects known as VAP and creation of additional lone pair on one of the chalcogen atoms \((C_1^-)\). Here \(2\Delta \geq U_{LP}\), where \(U_{LP}\) is the correlation energy if the electron is placed in a single localized LP orbital.
Chapter 1: Amorphous Semiconductors and Their properties

<table>
<thead>
<tr>
<th>Configuration</th>
<th>p-level occupation</th>
<th>Energy/configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C^0_2 )</td>
<td></td>
<td>(-2E_b)</td>
</tr>
<tr>
<td>( C^0_3 )</td>
<td></td>
<td>(-2E_b + \Delta)</td>
</tr>
<tr>
<td>( C^+_3 )</td>
<td></td>
<td>(-3E_b)</td>
</tr>
<tr>
<td>( C^-_3 )</td>
<td></td>
<td>(-E_b + 2\Delta + U_{\sigma^*})</td>
</tr>
<tr>
<td>( C^0_1 )</td>
<td></td>
<td>(-E_b)</td>
</tr>
<tr>
<td>( C^-_1 )</td>
<td></td>
<td>(-E_b + U_{LP})</td>
</tr>
</tbody>
</table>

Figure 1.6. The KAF model of structure and energies of simple bonding configurations in chalcogens. In configurations, straight lines represent bonding (\(\sigma\)) orbitals, lobes represent the lone-pair (LP) orbitals, and large circles represent the anti-bonding (\(\sigma^*\)) orbitals. The arrows indicate the spin state of the electrons. Energies are given using LP energy as zero [44].

The formation of defect species are likely to occur during the glass transition and due to their low creation energy, relatively high density of charged defects will be present in thermal equilibrium at \(T_g\), which will be frozen-in on quenching to form a glass [14]. Hence, the glass structure for \(T < T_g\) would retain the thermodynamic equilibrium number of defects appropriate to \(T = T_g\) [45]. If \(G_f\) is the free energy of creation of a defect, and \(N_0\) is the number of sites in the solid, then the defect concentration (N) will be
The lowest temperature at which the defects anneal away in the glass is the glass transition temperature $T_g$ and density of defects depends on $G_f$ & $T_g$. Further, it is also suggested that the $C_{3}^{+}$ & $C_{1}^{-}$ centers are randomly distributed in materials having high $T_g$ and large dielectric constants ($\varepsilon$). In materials having low $\langle r \rangle$, relatively small $\varepsilon$ and low $T_g$, a random distribution is unlikely and the Coulomb attraction between $C_{3}^{+}$ & $C_{1}^{-}$ leads to a significant density of Intimate Valence Alternation Pairs (IVAP’s) [44].

1.6. Chalcogenide glasses

1.6.1. Introduction

The elements occupying column VI-A of the periodic table – Sulphur, Selenium and Tellurium are known as chalcogens due to their ‘ore forming’ tendency. Chalcogenide glasses are compounds, which contain at least one or more chalcogen elements, often combined with semimetals. The chalcogenide glasses have attracted much interest for various reasons. First, they can be prepared in amorphous form in a variety of ways [14], either as vapor-deposited thin films or as melt-quenched glasses and also they form glasses continuously over wide range of compositions. Their physical properties vary in a continuous fashion; and they exhibit a unique behavior like switching etc., which find numerous potential technological applications.

1.6.2. Preparation of Amorphous Chalcogenides

Chalcogenide glasses can be prepared by various techniques like furnace cooling, melt quenching, splat quenching, vapor condensation, etc. Figure 1.7 shows the generally adopted methods of glass preparation in which the cooling rates differ over a wide range and consequently materials of varying glass forming ability can be prepared in the amorphous state.
Chapter 1: Amorphous Semiconductors and Their properties

| 1 : Furnace | 3 : Melt | 5 : Cold Substrate |
| 2 : Quartz Tube | 4 : Water at 0 °C | 6 : Vapor Source |

Figure 1.7. *The various methods of forming amorphous solids: (a) Furnace cooling (b) Moderate quenching and (c) Condensation from the gas phase.*

**(a) Furnace cooling:** A melt is allowed to cool slowly by simply turning off the furnace (figure 1.7(a)). The furnace cooling with a typical cooling rate of the order $10^{-4}-10^{-5}$ K/Sec is employed to prepare samples which have a high glass forming tendency such as SiO$_2$, As$_2$Se$_3$ etc.

**(b) Melt-quenching:** The chalcogenide bulk glasses in general are obtained by quenching the melt in ice-water or NaOH + Ice-water mixture as shown in figure 1.7(b). Typical characteristic cooling rates for melt quenching are in the range of $10^{-1}$-$10^{-5}$ K/Sec.

**(c) Vapor-condensation technique:** This technique is used to obtain amorphous chalcogenides in thin film form. In vapor deposition, the evaporated material is allowed to impinge upon the surface of a cold substrate, and thereby leading to the condensation of atoms on the surface as shown in figure 1.7(c). The amorphous structure is quenched in, if conditions are suitable to avoid the crystalline configuration; Ge, Si, etc, can be made as amorphous films only by vapor condensation techniques [15].
1.6.3. Phenomenon of Glass Transition and Glass Forming Ability (GFA)

When a liquid is allowed to cool, one of the following two events may occur. Either crystallization (process) may take place at the melting point $T_m$, or else the liquid will become “super-cooled” for temperatures below $T_m$, becoming more viscous with decreasing temperature, and may ultimately form a glass [14]. These changes can be observed quickly by monitoring the volume as a function of temperature and a typical plot is shown in figure 1.8 [15]. The crystallization process is manifested by a sudden change in volume at $T_m$ leading to a discontinuity in the volume $V(T)$, which is shown by path (a) in figure 1.8. Whereas glass formation is characterized by a gradual break in slope. That is, if the liquid is rapidly cooled so the crystallization is avoided, it may become super-cooled and follows path (b). The super-cooled liquid eventually transform into a glassy solid when the viscosity reaches around $10^{13}$ Poise. This event is known as glass transition, which is not a thermodynamic phase transition. The temperature region over which this transformation occurs is termed as the glass-transition temperature ($T_g$).

Similar behavior would also be exhibited by other extensive thermodynamic variables, entropy $S$, and enthalphy $H$. Since the transition to the glassy state is a continuous, and hence glass-transition temperature is not well defined. The glass transition reaction is a rate-dependent process and the thermal history of the sample determines the magnitude of glass transition temperature. Further, the glass transition is a second order thermodynamic phase transition, during which the second derivatives of volume, entropy, etc., show a discontinuous change [46].

The process of liquid $\leftrightarrow$ glass/crystal transition is always associated with a change in the accessible degrees of freedom of atomic motion which is manifested as a change in the specific heat ($C_p$). Figure 1.9 (a) shows $\Delta C_p$ for both liquid $\leftrightarrow$ crystal and liquid $\leftrightarrow$ glass transitions. It can be noted from figure 1.9(a) that a divergence is seen in the specific heat ($C_p$) at the freezing point ($T_f$) due to the latent heat associated with the crystal-melt transition. However, no such singularity accompanies the glass-liquid transition.
Figure 1.8. The volume-temperature relationship for a typical glass forming material. Volume-Temperature curves showing the two possible paths of cooling a Liquid melt to (a)crystalline state and (b) amorphous solid state [15].

Figure 1.9. A schematic illustration of the temperature dependence of (a) the specific heat $C_p$, and (b) the specific entropy, $S$, of a liquid, super-cooled liquid and the glass. Glass 1 (dashed curve) represents the state resulting from a cooling rate faster than that used to produce glass 2 [57].
transition. There are several models proposed or developed for explaining the phenomenon of glass transition \((T_g)\) in super-cooled liquids. Such as the configurational entropy model, free volume model, cluster model, and potential barrier model, stochastic agglomeration theory (SAT) model etc. [47-56].

1.6.4. Glass Forming Ability (GFA)

The glass forming tendency (GFT) or glass forming ability (GFA) has been a subject of much interest due to the technological importance of the composition dependent glassy materials. Numerous factors are believed to decide the GFA of a particular glassy material. On the basis of structural, thermodynamic and kinetic factors, various models have been proposed to understand the origin of glass formation. However, there is no structural rule, which may be used universally to predict GFA in any given system.

In the glassy chalcogenides, important parameters like, the compound formation and the resulting atomic structure, viscosity of the melt, cooling rate and the frustration in a multicomponent melt are found to influence the GFA [58]. The GFA is said to increase with covalency of the additive element and decrease with its size [59]. Further, efforts have been made by Phillips to understand the composition dependency of GFA on the basis of percolation in network rigidity, using constraint theory [60,61]. With respect to composition, the GFA decreases with increasing atomic mass. The GFA of elements belonging to a particular column in the periodic table follows the following order [62, 63]. The GFA of

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

Concerning cooling rate, many oxide glasses can be formed even with cooling rate slower than 1K/hr, whereas most of the metallic glasses require cooling rate of the order of \(10^6\)K/sec [14, 15].
1.6.5. Structural Network in Glassy Chalcogenides

Knowledge of the structural rearrangement of atoms in a glassy material is very essential for understanding physical or chemical properties. The first attempt to understand the atomic structure of glassy semiconductors was made by Zachariasen [64]. According to Zachariasen’s model, a substance can readily form an extended three dimensional network lacking periodicity if the coordination polyhedra in the glass and the corresponding crystal are similar and the energy content in the glass is comparable to that of the crystal. There are several other models have been proposed for topologically disordered systems, in order to understand the essential features of their atomic structure.

1.6.5.1. Homogeneous Continuous Random Network (CRN) model

The earliest attempt to understand atomic arrangement in glassy semiconductors was developed by Zachariasen with a random network hypothesis [64]. The assumptions made in Zachariasen’s Continuous Random Network model (CRN) are the following:

(a) The coordination of the constituent atoms satisfies the 8-N rule [26], where N represents the column in the periodic table to which the element belongs.

(b) The local structure in glassy semiconductors is not completely random; a considerable degree of short range order (SRO) present in these materials. The nearest neighbour distances (bond-lengths) in the glassy and the corresponding crystalline state are nearly the same; the bond lengths are allowed only < 1% variation, whereas the bond angles are allowed to vary about ±10% [15].

(c) Both structures are ideal and do not admit any defects such as over-coordinated atoms or under-coordinated dangling (unsatisfied) bonds [15].

The two dimensional CRNs constructed on the basis of above principles are shown in figure 1.10 for two representative glasses. According to the CRN model, glasses can form topologically disordered 3-d. Later, the atomic structure of different glassy semiconductors, such as amorphous Si [65], glassy Se [66, 67] and many other multicomponent glasses [14, 68] have been modeled based on the CRN features.
1.6.5.2. The Random Covalent Network (RCN) and Chemically Ordered Covalent Network (COCN) models

The Random Covalent Network (RCN) and the Chemically Ordered Covalent Network (COCN) models are variants of the CRN model which have been proposed to explain the local structure of amorphous semiconductors [69]. The RCN model is based on the statistical distribution of bonds among atoms whereas the COCN model is based on the relative bond energies.

In RCN model, the distribution of the bond types is purely "statistical" and is determined only by the local coordinations $n_a$ and $n_b$ and the concentration variable $x$ of the constituent atoms and neglects any preferential ordering effects. In binary alloy system of the type $A_xB_{1-x}$, RCN model admits $A$-$A$, $A$-$B$ and $B$-$B$ bonds at all compositions except at $x=0$ and $x=1$. According to this model, the distribution of the three types of bonds for IV-VI alloy system (e.g., $A$=Ge, $B$=Se) is given by
Chapter 1: Amorphous Semiconductors and Their properties

\[ N_{AA} = \frac{4(1-x)^2}{(2-x)}, \quad N_{AB} = \frac{4x(1-x)}{(2-x)}, \quad N_{BB} = \frac{x^2}{(2-x)} \]  

(1.6)

The COCN or CON model emphasizes on the relative bond energies of various constituents. This model favors higher energy bonds over those with lower energy; this approach is based on the assumption that heteropolar bonds are favored over homopolar bonds. Since the heteropolar bonds A-B are favored; a completely chemically-ordered phase thus occurs at the stoichiometric composition

\[ x_c = \frac{n_a}{(n_a + n_b)} \]  

(1.7)

In contrast to the RCN model, only A-A and A-B bonds are allowed for A-rich compositions \( (1 > x > x_c) \) and only B-B and A-B bonds for \( 0 < x < x_c \). The bond-counting statistics for the RCN and COCN model are schematically depicted in figure 1.11.

\[ \text{Figure 1.11. Bond counting statistics for a } A_{1-x}B_x \text{ system with 4:2 coordination [55].} \]
1.6.5.3. Cluster-Model (Inhomogeneous)

This model essentially considers a network to consist of covalently bonded groups of atoms held together by weak intermolecular forces like Van der walls or hydrogen bonding. Glassy materials such as \(\text{a-SiO}_2\), \(\text{a-As}_2\text{Se}_3\), \(\text{a-GeSe}_2\) etc., with low-average coordination number \(\langle r \rangle\), in the range of \(2 \leq \langle r \rangle \leq 2.4-2.6\) are generally understood using cluster models [70]. Unlike the CRN models, the basic criterion of GFA is related to condition of mechanical stability (constraints v/s freedom) rather than the condition of chemical order.

1.6.6. Network Topological Thresholds in Glassy Chalcogenides

It has been found that the addition of higher coordinated atoms to a glassy network containing predominantly chalcogen atoms results in gradual transformation of a flexible (floppy) and weakly cross-linked chains to a rigid three dimensional network glasses. This transition occurs when the composition of cross-linking agents reaches a threshold value, and that good glass formation could be expected near this threshold [60, 71]. In covalent network chalcogenide glasses, when the composition is varied continuously, many physical properties exhibit distinct changes at certain specific compositions, known as the Rigidity Percolation Threshold (RPT) or Mechanical Threshold (MT) (also known as Stiffness Threshold) and the Chemical Threshold (CT) [72-74]. Rigidity percolation threshold is understood on the basis of a constraints model which has been developed by extending the CRN approach, whereas chemical threshold is a direct consequence of COCN or CON model [60, 61, 71, 75]. RPT deals with the elasticity of the network, the balance between mechanical constraints on the network and its degree of freedom, whereas CT deals with chemical ordering in a chalcogenide network.

1.6.6.1. Rigidity Percolation Threshold or Mechanical Threshold

In 1979, J.C. Phillips proposed a model based on the constraints theory to understand the evolution of the local structure and glass forming tendencies in
Chapter 1: Amorphous Semiconductors and Their properties

chalcogenide network glasses as a function of composition [60, 61, 71, 75]. Phillips considered the covalent bonding as a mechanical constraint experienced by the atoms in order to explain the ability for making a glass. The degree of cross-linking in the covalent network glass is expressed in terms of a mean/average coordination number \( \langle r \rangle \). The coordination number of atoms that are present in the glass, allows the construction of the \( \langle r \rangle \), which in some sense is the coordination of atom forming a structure whose topology is similar to that of the system [14]. For a ternary alloy of the type \( \text{A}_x\text{B}_y\text{C}_{1-x-y} \), \( \langle r \rangle \) is,

\[
\langle r \rangle = x \, r(A) + y \, r(B) + (1-x-y) \, r(C)
\] (1.8)

In general, if the total number of atoms is \( N \) and there are \( n_r \) atoms with a coordination \( r \) \( (r=2,3,4) \), then

\[
N = \sum_{r=2}^{4} n_r
\] (1.9)

The average coordination \( \langle r \rangle \) is defined as

\[
\langle r \rangle = \frac{\sum_{r=2}^{4} r \, n_r}{N}
\] (1.10)

Further, Phillips proposed a connection between glass-forming ability (GFA) and the average coordination number [60]. The idea is that the GFA is maximized when the number of mechanical constraints per atom in each atom, \( N_c \) is equal to the number of degrees of freedom per atom (\( N_d \)), which is essentially the dimensionality of the network. Thus the condition for optimal glass formation is

\[
N_c = N_d
\] (1.11)

A system with more constraints than \( N_d \) is overconstrained and cannot easily form a glass.

In a chalcogenide covalent network, the constituent atoms are constrained due to the fact that the bond lengths and angles are well defined, although there are small
Chapter 1: Amorphous Semiconductors and Their Properties

departures from the equilibrium position. The strain potential energy of these deviations can be well described by the Valance Force Fields (VFF) model in which strain potential energy (V) or Kirkwood or Keating potential (figure 1.12) as sum of contributions from bond-stretching and bond-bending forces,

\[ V = \left[ \frac{\alpha}{2} (\Delta l)^2 + \frac{\beta}{2} (\Delta \theta)^2 \right] \]  \hspace{1cm} (1.12)

Where \( \alpha \) and \( \beta \) are the bond-stretching and bond-bending force constants, and \( \Delta l \) and \( \Delta \theta \) are small deviations from equilibrium in bond-length and bond-angles respectively.

Figure 1.12. The Keating potential bond-stretching \( \alpha \) and bond-bending \( \beta \) terms [76]

Thorpe estimated the number of constraints using the Maxwell counting [71]. According to this counting, each \( r \) coordinated atom is associated with \( \frac{r}{2} \) bond-stretching constraints, since there are \( r \) bonds, each of them are shared by two atoms. In each atom, there are \( 2r-3 \) constraints that come from the angular forces. The total number of constraints acting on the system is,

\[ \sum_{r=2}^{d} n_r \left[ \frac{r}{2} + (2r - 3) \right] \]  \hspace{1cm} (1.13)
The fraction of floppy modes with respect to the degrees of freedom is,

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

(1.14)

where \( \langle r \rangle \) is defined in equation 1.10.

When \( \langle r \rangle = 2 \) (e.g., Se-chains), \( f \approx \frac{1}{3} \); i.e., one third of all the modes are floppy. When atoms with higher coordination (>2) are added as a cross-links to the network, \( f \) decreases and goes to zero at \( \langle r_c \rangle = 2.4 \) and the network goes through a phase transition from floppy to rigid.

Thus, at a critical average coordination number \( \langle r_c \rangle = 2.4 \), wherein, the no of degrees of freedom per atom \( (N_d) \) equals the no of constraints \( (N_c) \) acting, a mechanical equilibrium is established.

**Figure 1.13.** The floppy and rigid regions in the two types of covalent random networks described in text [71].
floppy matrix. At $\langle r \rangle = \langle r_\varepsilon \rangle = 2.4$ the rigid clusters coalesce and there is a percolative transition in the network from a floppy polymeric glass to a rigid amorphous solid. Further, for $\langle r \rangle > \langle r_\varepsilon \rangle$, the network is over-coordinated or over-constrained and rigid in nature with few floppy inclusions. The polymeric floppy and rigid glasses are shown in figure 1.13. The critical average coordination number $\langle r_\varepsilon \rangle = 2.40$ is commonly referred to as the Rigidity Percolation Threshold (RPT) or Mechanical Threshold (MT) or Stiffness Threshold (ST). The signatures of the rigidity transition or stiffness transition have been observed in compositional variation of different properties of many chalcogenide glassy systems [77-79].

The above constraint counting theory fails when one-fold coordinated (OFC) atoms like halogens are present because when $r = 1$, number of angular forces ($2r-3$) becomes equal to -1, instead zero. The constraint theory has been extended to chalcohalide glasses and the corrected or modified fraction of floppy modes with respect to the degrees of freedom is

$$\begin{align*}
\hat{f} &= \left[ \frac{3N - \sum_{r=2}^{4} n_r \left( \frac{r}{2} - (2r - 3) \right) - n_1}{3N} \right] \\
\hat{f} &= 2 - \frac{5}{6} \langle r \rangle - \frac{n_1}{N}
\end{align*}$$

(1.16)  

(1.17)

The rigidity transition in these glasses takes place at a lower critical average coordination number $\langle r_\varepsilon \rangle$, which is given by

$$\langle r_\varepsilon \rangle = 2.4 - 0.4 \left( \frac{n_1}{N} \right)$$

(1.18)

Where, $\left( \frac{n_1}{N} \right)$ is the ratio of OFC atoms to the total number of atoms. The rigidity transition takes place at a lower average coordination $\langle r \rangle$ because the OFC-atoms play no role in the network connectivity.
Phillips-Thorpe formulation based purely on short range interactions was later modified by Tanaka [80-81]. He argued that the chalcogenide glassy network possess a layered structure and hence medium-range interactions have to be considered in order to effectively understand the topological changes in these glasses as \( \langle r \rangle \) is varied. Further, he showed that when medium-range interactions and the formation of layered structure are included, the threshold value shifts to \( \langle r \rangle = 2.67 \).

It has been suggested by Tanaka that there can be a shift in the MT value from \( \langle r_e \rangle = 2.40 \), in certain glassy systems [80-81]. In systems with a planar network,

\[
N_{CO} = \frac{r}{2} + (r - 1)
\]  

Using constraints counting theory,

\[
N_{CO} = N_d
\]  

\[
\therefore \frac{r}{2} + (r - 1) = 3
\]

\[
\langle r_e \rangle = 2.67
\]

The transition occurring in the network at \( \langle r_e \rangle = 2.67 \) is suggested to form a two dimensional to a three dimensional structure.

1.6.6.2. Extended Rigidity Transition and Self-Organized Glassy Network

The recent theoretical and experimental investigations revealed that in certain chalcogenide glassy systems, the rigidity transition (stiffness transition) may span over a range of compositions/average coordination numbers [82-84]. In these systems, RPT or MT occurs as a two stage process, namely transition from a floppy polymeric phase to isostatically rigid phase and from an isostatically rigid to a stressed rigid phase. The region constituting the isostatic rigid phase forms the intermediate or Boolchand's phase,
which is also known as the thermally reversing window [82], wherein the sample is rigid but without any stress [82-86].

The glass compositions residing within the intermediate phase are supposed to be self organized and stress-free and width of the intermediate phase is a measure of the self organization in the glassy network [84]. Also, glasses in the intermediate phase possess some unusual properties like near absence of a latent heat of melting and possess configurational entropy, which is nearly same as those of the corresponding melts, as revealed by the Modulated Differential Scanning Calorimetric (MDSC) measurements. The occurrence of intermediate phase has been experimentally observed in variety of glassy systems such as Ge-Se [87], Ge-S [87], As-Se [82], As-Se-Ge [88], P-Ge-Se [89].

1.6.6.3. Chemical Threshold: $x_c$

According to CRN model, bonds are distributed continuously in a purely statistical manner and 8-N rule is satisfied for all the components of the chemical system. This model works well when the difference in bond energies in a system is small. If the relative strengths of the bonds differ significantly in the system, the heteropolar bond being the strongest, the system will tend to an ordered state. The corresponding composition will be highly stoichiometric with only heteropolar bonding leads to a maximum chemical ordering occurring at critical composition $x_c$. The composition $x_c$, at which chemical stability is said to be highest is often referred to as chemical threshold (CT) of the glassy system. This chemical ordering has been explained by the Chemically Ordered Covalent Network model (COCN) [30, 69, 90]. For example, in Ge$_x$Se$_{1-x}$ glassy system, as the Ge concentration increases, the network is more cross-linked and this entails the formation of heteropolar bonds of Ge-Se. At a particular value of $x$, the network has only heteropolar bonds and is said to be fully chemically ordered; it is known to have reached the chemical threshold (CT). That is when the valence requirements of divalent- Se are completely satisfied by tetravalent- Ge.

$$2(1 - x_c) = 4x_c \quad (1.23)$$
$$x_c = 0.33 \text{ or } \langle r \rangle = 2.67 \quad (1.24)$$
Similarly for As$_x$Se$_{1-x}$ glassy system, the CT occurs at $x_c = 0.40$ or $\langle r \rangle = 2.40$. The physical implication of CT is that, glass formation is most difficult for this composition in a given glassy system, as the glass (at CT) is energetically closest to the corresponding crystalline state [91-92].

1.6.7. Defect States in Glassy Semiconductors

The RCN, COCN and Cluster models are proposed to understand the structural network in chalcogenide glassy semiconductors, consider an ideal glassy network without any defects. That is, all the constituent atoms satisfy their valence requirements and supposed to obey 8-N rule. Although, free from the constraints of periodicity, glassy semiconductors posses a wide range of defects in terms of over-coordinated atoms, dangling bonds etc. These defects form an inseparable part of chalcogenide glasses and control their electrical, optical and optoelectronic properties [93]. Among the several types of defects present, the charged defects are the most important in chalcolgendie glasses [38]. Based on the Anderson's idea [40], Street and Mott proposed a model to elucidate the nature of defects in chalcogenide glassy semiconductors [39] and it has been discussed in detail in the previous subsection 1.5.1. Later, another model was proposed by Kastner, Adler and Fritzche (KAF) [44], which was quite successful in explaining most of the properties exhibited by chalcogenide glasses and is discussed in detail in the previous subsection 1.5.2.

1.6.8. Doping in Chalcogenide Glasses

Dopants in glassy chalcogenide semiconductors act as network modifiers and can influence transport properties in large scale. Considerable amounts of thallium, antimony, potassium, alkali metals, silver, copper etc., may be introduced into chalcogenide glasses. These metal additives act as network modifiers. On the other hand halogens as dopants in chalcogenide glasses act as network terminators. For example, singly coordinated halogen substituted for two-fold coordinated chalcogen results in the de-polymerized structure [94-95].
1.7. High Field Behavior and Electrical Switching

The normal behavior of a metal or a semiconductor is the linear proportionality between the applied voltage (V) and the induced current (I), which is the classic ohm's law behavior. This behavior is common in many passive and active devices forms a basis for the well-established linear system behavior. Certain materials in many different forms cannot withstand sufficiently high electric fields ($10^6$ V/cm) and exhibit a non-linear electrical behavior [96-97]. This leads to a phenomenon of electrical switching, in which a material switches to a high conducting 'ON' state from a low conducting 'OFF' state under the application of a suitable electric field. However, in insulating materials, such high electric field leads to a destructive breakdown. The discovery of nondestructive switching in some chalcogenide alloys by S.R. Ovshinsky [97-99] has provoked enormous interest in the electrical switching behavior of amorphous semiconductors.

A variety of materials, crystalline and amorphous, exhibit non-destructive electrical switching and negative resistance phenomenon at higher fields. In general, the negative resistance effects can be classified into the following six types [7-8] as shown in figure 1.14:

(a) Voltage controlled negative resistance (VCNR)
(b) Voltage controlled negative resistance with memory
(c) Current controlled negative resistance (CCNR)
(d) Current controlled negative resistance with memory
(e) Threshold switching
(f) Memory switching
Figure 1.14. Six possible types of non-ohmic behavior observed in amorphous materials. (a) VCNR, (b) VCNR with memory, (c) CCNR, (d) CCNR with memory, (e) threshold switching and (f) memory switching [7].

(a) Voltage controlled negative resistance (VCNR)

In a VCNR device, the material starts from a low resistance state and exhibits a ohmic behavior up to a critical voltage or threshold voltage $V_T$. Above $V_T$, material passes through a negative resistance region to reach a high resistance state as shown in figure 1.14a. Further, I-V characteristic is reversible (threshold) in a VCNR device [7] and is also known as N-shaped instability.

(b) Voltage controlled negative resistance with memory

In a VCNR device with a memory, both a low-resistance and a high-resistance state once reached is retained even when the voltage is reduced as shown in figure 1.14b.

(c) Current controlled negative resistance (CCNR)

In a CCNR device, the voltage increases with current initially. At a threshold current $I_T$ (corresponding to $V_T$), the voltage starts decreasing with increasing current,
passing through a negative resistance zone, to reach a low resistance state. If the current is reduced, the characteristic is retraced as shown in figure 1.14c and I-V characteristic of CCNR is also called as S-shaped instability.

(d) Current controlled negative resistance with memory

In CCNR device with memory, low resistance state once set, is retained even under zero bias condition. That is, two distinct states exist; a high resistance state and a low resistance state, even in the absence of an applied field (figure 1.14d).

(e) Threshold switching

Threshold switching device is similar to that of a CCNR device. However, they do not have a stable operating point between the high resistance OFF state and the low resistance ON state as shown in figure 1.14e. At the threshold current $I_T$ (corresponding to $V_T$), the device switches from high resistance OFF to a low resistance ON state in a very short time. It supports a high value of current though it in the ON state, without passing through a negative resistance state. In a threshold switching device, the low resistance ON state is retained only if the current is maintained above the holding current ($I_h$). If the current is reduced below $I_h$, the device switches back to high resistance OFF state retracing its original path. That is, behavior is reversible as depicted in figure 1.14e and is known as threshold switching or Ovshinsky switching.

(f) Memory switching

Memory switching samples once switched remain in the low resistance ON state even if the current is reduced to zero as depicted in figure 1.14f. That is, in memory devices, the ON state sets in permanently and the current can be brought down to zero without affecting the behavior of the ON state. However, the OFF state can be restored by passing a strong pulse of current. This behavior is known as memory switching.
Chapter 1: Amorphous Semiconductors and Their properties

1.7.1. Electrical Switching in Glassy Chalcogenides

In the year 1968, Ovshinsky discovered the electrical switching phenomenon in chalcogenide glasses, which find several technological applications such as in memory devices [97]. Electrical switching in chalcogenide glasses takes place when an appropriate field corresponding to threshold voltage $V_T$ (known as threshold or switching field $E_T$) is applied, the glass switches from low conducting OFF state to a high conducting ON state [97]. Glassy chalcogenides, which exhibit switching, are classified into threshold (reversible) and memory (irreversible) type based on their response to the applied electric fields. The distinction between the two classes lies in the way they respond to the removal of the electric field, which enables them to switch. On the removal of the switching field, threshold switching glasses revert to the OFF state whereas memory switches remain locked to the ON state. Thus the threshold switches are monostable and return to the initial OFF state, while the memory switches are bistable and get latched permanently to ON the state.

1.7.1.1 Mechanisms of Threshold and Memory Switching in Chalcogenide Glasses

There are several models proposed to understand the switching effects in glassy chalcogenides. In general, threshold and memory switching in chalcogenide glasses have been discussed on the basis of electronic and thermal models respectively.

1.7.1.1.1. Threshold switching

The threshold switching in glassy chalcogenides is primarily electronic in nature. The models proposed for threshold switching process are as follows: (i) purely electronic (ii) space charge mechanism (iii) Electro-thermal mechanism.

(i) Purely electronic model

This model proposed by Adler and Peterson [9,100-102], is based on the field-induced filling of positively and negatively charged defects called valence alternation
pairs (VAP’s) \( (G^-_T \text{ and } C^+_T) \). Threshold switching glassy chalcogenides are expected to have large densities \( (10^{17}-10^{19} \text{cm}^{-3}) \) of VAP’s. Under sufficiently large electric fields, carriers are excited and field generated electrons and holes fill these charged traps. Once all the charged defects states are filled, the life time of the further excited charge carriers increase sharply to a value much larger than that needed to cross the thickness of the sample. Increase in lifetime as well as carrier concentration increase the conductivity \([103-104]\) leading to ON state. This leads to a drop in the voltage and the associated switch to the conducting ‘ON’ state. This process is clearly reversible and hence, threshold switching is also referred to as reversible.

**(ii) Space-charge mechanism**

Henisch [105], Henisch et.al [106] and Lucas [107] suggested a qualitative explanation for threshold switching process and is based on double carrier injection mechanism. It is suggested that both electrons and holes are injected by the applied electric field. According to Henisch model, a negative space charge builds up near the cathode and a positive space charge builds up near the anode due to the trapping of injected carriers. The regions of space charge will limit the current flow in the vicinity of the electrode and the field will be redistributed, decreasing near the electrodes and increasing at the center. As the applied field is increased, more charges are injected and the space charge regions grow until eventually they meet and overlap, resulting in an unstable state. When the recombination centers are filled, the carrier lifetimes and hence the electron and hole conductivities increase. In the region of overlapping charge, the material is electrically neutral; the conductivity in the center and the field near the electrode increases. Electrons and holes are accelerated rapidly across the neutral region and due to the enhanced field, injection of carrier at the electrode increases. Both effects increase the rate at which space charge overlap occurs i.e., there is a positive feedback and hence an unstable situation. Since the space charge has been neutralized and traps are filled, the conductivity increases leading to the conducting ‘ON’ state.
(iii) Electro-thermal mechanism

A.C. Warren [108] proposed an electro-thermal mechanism for understanding the threshold switching process. Though an electronic process initiates switching, a current channel will form upon switching and results in a considerable temperature rise in this channel as the Joule heat is dissipated in a rather small volume. The electronic process must include these thermal effects and associated thermal time constants under certain circumstances. By obtaining the numerical solution to the dynamic heat balance equations and upon substituting the appropriate material parameters i.e., specific heat, thermal conductivity, and electrical conductivity of the material [109], it has been possible to predict the non-ohmic pre-switching behavior of the material. Based on the above considerations, it has been suggested that there can be a temperature rise of several hundred degrees along the conducting channel before the current shows any substantial changes.

1.7.1.1.2. Memory switching

In general the memory switching is believed to be dominated by the thermal process. Memory switching in chalcogenide glasses is considered to be a consequence of a phase transition of the material from the amorphous to crystalline state [9]; in the crystalline state the conduction is higher as the disorder is significantly lesser. It is believed that memory switching occurs in those glassy chalcogenides in which the cross linking atoms are too few in number. Such glasses have lesser thermal stability [9] and on application of a high electric field or heating leads to the crystallization of these glasses. The crystallization of the chalcogenide glasses into the fine filaments, which is responsible for memory switching, is believed to be caused by the Joule heating [8] and the resultant excess carrier concentration in the current path due to a large electric field. The formation of crystalline conducting channel in a memory chalcogenide glass during switching has been confirmed by electron microscope and optical reflectivity investigations [8].

35
Figure 1.15. The cyclic process which succeeds after the initiation of switching and leads to memory switching.

Figure 1.15 illustrates the electro-thermal process which occurs after the initiation of switching. The increase in conductivity after switching leads to an increased power dissipation in the sample, which in turn causes a rise in the temperature of the conducting filament due to Joule heating. The temperature increase in the conducting filament leads to a higher conductivity, more power dissipation and further increase in temperature. This cyclic process can eventually trigger the phase change and memory switching in certain chalcogenide glasses.

1.7.1.2 Factors Deciding the Type of Switching Exhibited by Chalcogenide Glasses

There are several factors which decide whether a chalcogenide glass will exhibit memory or threshold type electrical switching:

(a) The ON state current

If the current flowing through the conducting channel is limited below a certain value (which is different for different glassy systems), a threshold behavior is seen. However, the sample may exhibit memory behavior at higher ON state currents [110].
(b) The thermal stability of the glass

Samples which are prone to an easy divitrification are expected to show the memory behavior even at lower ‘ON’ state currents.

(c) Thermal diffusivity

The temperature rise in the conducting filament is also decided by the rate at which heat is dissipated 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 probable compared to those with higher thermal diffusivity [111].

(d) Network topological effects

The network connectivity and the rigidity (which are determined by the coordination number of the constituents), network topological thresholds (such as rigidity percolation and chemical threshold), etc., have been found to play a crucial role in the electrical switching behavior of glassy chalcogenides. This aspect is discussed in more detail in the next sub-section 1.7.1.3.

1.7.1.3. Electrical Switching and Topological Thresholds in Chalcogenide Glasses

The I-V characteristics are known to be a reflection of the microscopic properties of a system. The switching field is found to be influenced by the local structure of a glass, which is determined by the coordinations of the atoms. In chalcogenide glasses, the atomic network is characterized by the average coordination number of atoms $\langle r \rangle$. For $\langle r \rangle < 2.40$, the structure of a glass is known to be elastically floppy while above that it is elastically rigid [71]. The switching field increases with rigidity of the atomic network [112]. Using this technique RPT has been determined in simple binary systems such as As-Te [113] and Al-Te [114] and both RPT and CT in ternary systems like Al-Ge-Te [115] and Ge-As-Te [112]. Whereas, chemical ordering signified by CT has the opposite effect on switching; it reduces switching field [112].
Electrical switching is one of the best characterizing tool for identifying the network topological thresholds namely the RPT and CT of a chalcogenide glassy system. Investigations on a wide variety of chalcogenide glasses indicate that the composition dependence of switching voltages of both memory and threshold switching glasses exhibit specific signatures at both the RPT and CT of the system [112,116-120]. In general, the compositional variation of $V_j$ has been found to exhibit either a maximum or a sharp slope change at the RPT and local minimum at CT.

1.7.1.4. Switching Parameters in Chalcogenide Glasses

In the threshold and memory switching chalcogenide glasses, the switching process is initiated when the voltage drop across the sample exceeds the threshold voltage $V_T$, and the material changes its resistivity state, within about $10^{-10}$ sec [8]. The following important device parameters provide the basis for the understanding of the switching mechanisms in chalcogenide glasses:

(i) **Switching voltage ($V_T$)**

The switching voltage or threshold voltage ($V_T$) is defined as the voltage at which the threshold/memory material switches along the load line to the high conducting 'ON' state. It depends on the sample thickness/electrode separation, temperature, resistivity of the material and nature of excitation (DC, Pulse, ramp) etc. It is therefore important to specify in each case the conditions under which $V_T$ is measured.

(ii) **Switching time ($t_s$)**

In both threshold and memory switching materials, once the switching is initiated, the material changes state within a time interval of $10^{-10}$ sec [8]. This time is generally known as the switching time of the device.
(iii) **Delay time** \((t_d)\)

Glassy chalcogenides do not switch to the conducting state immediately as the threshold voltage is exceeded, but remains in the high resistance state for a period of time, known as delay time \((t_d)\). The delay time is the time interval between the application of voltage pulse \(V_p\) and the initiation of the actual switching process. The delay time is typically of the order of 10 \(\mu\) sec for a threshold device [8, 121]. Delay time decreases exponentially with the overvoltage [122] and it attains values of the order of \(10^{-9}\) sec when the voltage applied is about 50% higher than the threshold voltage [121]. Fluctuations in the delay time are observed when the overvoltages are less than 20% of threshold voltage \(V_T\) [122].

(iv) **Lock-on time** \((t_{io})\)

When a memory sample switches to a low resistance ‘ON’ state, after the delay time ‘\(t_d\)’, it should be kept in the low resistance state for a minimum period, known as lock-on time \((t_{io})\) to ‘set’ the material in the memory state. This time period is called the Lock-on time [121,123,124]. Incase the switching process is initiated by a pulse and if the pulse width is less than the ‘\(t_d + t_{io}\)’, the memory switch will revert back to its initial high resistance ‘OFF’ state. The lock-on time depends on the applied overvoltage and is a characteristic of the sample. Typically the lock-on time is found to be higher than 100 \(\mu\) sec [122].

(v) **Recovery time** \((t_r)\)

In a threshold switch, after the sample is switched, a definite time is required by the sample to recover its initial state, and it is brought back to the high resistance state by reducing the current below holding current \(I_h\). A definite time is required for the sample to recover to its original state at a particular \(V_T\) and this time is known as the recovery time \((t_r)\) and is typically of the order of 1 \(\mu\) sec. If the sample is switched again within the recovery time, it switches to a lesser \(V_T\) [7,123,124].

39
(vi) **Set time**

It is the time required to ‘SET’ the device from the high resistance ‘OFF’ state to a conducting ‘ON’ state [8]. For memory switching, it is the sum of \( t_D \) and \( t_{IO} \).

(vii) **Reset time**

The reset time \( (t_r) \) is the time required to bring the device back to the initial high resistance OFF state by applying suitable current/voltage pulse. The reset time is important in the context of memory switching only.

**1.7.1.5. Factors Affecting the Threshold Voltage \( (V_T) \) of Chalcogenide Glasses**

(i) **Frequency**

At low frequencies, the rate of change of the applied voltage is very low and \( V_T \) is not affected due to quasi-equilibrium. Whereas, \( V_T \) drops drastically at higher frequencies because of the recovery time \( (t_r) \) [8].

(ii) **Temperature**

In both threshold and memory switching devices, threshold voltage \( (V_T) \) is found to decrease with increasing temperature [121]. The temperature dependence of the switching voltages is indicative of the thermal degradation of the switching device and is an important factor for characterizing the thermal stability of the material for device applications, as well as for understanding the switching mechanisms.

(iii) **Sample thickness**

Thickness dependence of switching fields can be indicative of the mechanism of switching involved. Kolomiets et. al.,[125] proposed that in thin films up to 10 \( \mu m \) thickness, the mechanism is electronic and above this thickness, thermal effects are found to involve in switching mechanism.
1.7.1.6. Application of Glassy Chalcogenide Switching Materials

In a memory device, once it is switched to a low resistance 'ON' state it can be retained permanently and it can be used to 'write' or register information. Thus, memory switches are of technological importance in making Read Only Memory (ROM) panels. Further, after switching in to the conducting 'ON' state, a memory switch can also be RESET (re-amorphized) to the initial high resistance 'OFF' state by the application of appropriate electrical/light pulses [97]. This fascinating feature has been used in making Non-Volatile Random Access Memories (NVRAM) [121]. Using the resettable memory switching, Phase Change Memories (PCM) based on chalcogenide glasses are being considered recently as a possible replacement for conventional NVRAMs and flash memories [126-128]. The main advantages of chalcogenide phase change memories are their capability to write/overwrite, lower operational voltages, large number of write/erase cycles, etc. The basic principle in phase change memories is the reversible transition between two structural (amorphous-crystalline) states in stable fashion.

Threshold switching is of great importance for fabricating binary logic (ON-OFF) elements. The switching times are long at $V_T$ in threshold (Ovshinsky) devices compared to the same in crystalline switching devices. However, when the voltages applied are increased 50% above the threshold voltage ($V_T$), the switching times drops to nanoseconds or lower, making them competitive. Threshold switches are also used as power conditioners, transient voltage suppressors etc., [129].

1.8. Objectives of the Present Work

The present thesis work essentially deals with studies on certain electrical and thermal properties of Thallium and Antimony doped Ge-Se glasses belonging to the III-IV-V-VI family of chalcogenide glasses. In the present work, two series of glasses, namely Ge-Se-Tl and Ge-Se-Sb, are chosen to study the effect of Thallium & Antimony doping on electrical and thermal properties of these glasses.
Chapter 1: Amorphous Semiconductors and Their properties

Thallium and Antimony doped Ge-Se glasses are chosen in this study, to investigate the role of these atoms in the network growth and switching behavior in chalcogenide glasses and subsequent effects of the same on the electrical and thermal properties.

Electrical switching and thermal studies have been undertaken on Ge-Se-Tl and Ge-Se-Sb glasses over a wide range of compositions. Studies have been made on the I-V characteristics and switching behavior of these samples to know the nature of the switching, dependence of switching voltages on other properties such as network connectivity, coordination of the constituents etc. Thermal analysis on these samples has been used to obtain glass transition and crystallization temperatures, specific heat capacity, relaxation enthalpy, glass forming ability, etc. Further, the compositional dependence of thermal and electrical properties of these glasses has been carried out to probe the existence of rigidity percolation threshold and the presence of an intermediate phase in these glassy samples.
References

Chapter 1: Amorphous Semiconductors and Their properties


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Chapter 1: Amorphous Semiconductors and Their properties

Chapter 1: Amorphous Semiconductors and Their properties


48
Chapter 1: Amorphous Semiconductors and Their properties