CHAPTER I

INTRODUCTION

1.1 Thesis Statement

By incorporating metallic additives like lead into the germanium telluride glassy systems, it is possible to study the properties of GeTe systems as a function of increase in Pb content. Earlier studies [Tohge et al., 1980; Tohge et al., 1987; Bhatia et al., 1988; Murugavel, et al., 1998] on chalcogenide systems have revealed that the metallic additives bring about a change in the carrier concentration from p to n. Present study of the Ge-Te-Pb systems showed no carrier type reversal with the increase in Pb content which is evident in the thermopower measurements. Thermal analysis using modulated differential scanning calorimetry (MDSC) revealed that the sample exhibited topological thresholds at two different compositions of Pb. Electrical switching studies also showed the topological thresholds. Photoconductivity measurements on both bulk and thin films measurements were done. The optical studies were done for thin film samples and the optical constants were evaluated as a function of wavelength using spectroscopic ellipsometer.

The motivation of the present work is manifold. Chalcogenide glasses are generally less robust, more weakly bonded materials than oxide glasses. They are insensitive to impurities with the Fermi level pinned at the center of the mid-gap, unlike the crystalline counterparts where special care has to be taken during their preparation. Both heteropolar and homopolar bonds are possible in chalcogenide glasses. The chemical bonding of the matrix is usually directional and covalent with halogens acting as chain or network terminators. The chalcogenide glasses are band gap semiconductors and are infrared transmitting.
Many distinct phenomena are observed in amorphous chalcogenides that are not usually noticed in crystalline chalcogenides which finds technological importance. To mention a few the first chalcogenide glasses to be commercially developed was $\text{As}_2\text{S}_3$ for passive, bulk optical components for the mid IR in the 1950's. Later, other sulphides and selenide glasses were developed, as well as selenide-telluride glasses for optical components for the far IR, which have since been exploited commercially. Applications of IR optics include energy management, thermal fault detection, electronic circuit detection, temperature monitoring and night vision. The wide IR window of chalcogenides and the high resolution of FTIR spectroscopy together permit remote sensing of gases/liquids using absorption due to fundamental vibration modes.

The photoinduced phase transition from amorphous to crystalline, and vice-versa, in chalcogenide glasses has formed the basis for optical mass memory applications. Thus a focussed laser writes information by inducing a localized phase transition and the data are read by utilizing the difference in reflectance between the amorphous and crystalline phases.

1.2 Amorphous Semiconductors – Introduction

The technological advancements and the progress made over the years in the development of devices made of crystalline materials are well known. Examples being transistors, microwave oscillators, lasers, etc. The major characteristics of a crystal are that its constituent atoms or molecules are aligned in ordered three-dimensional arrays that exhibit a long-range periodicity. The physical phenomena in these solids are well understood using quantum mechanics (David Adler., 1977) because of the mathematical simplifications that result from such periodicity. This understanding had eventually led to the development of solid state devices. In spite of these great successes the careful techniques of preparation and crystal growth necessary to fabricate devices based on crystalline materials have important economic drawbacks. The example of this is found in the fabrication of solar cells the reliability of which has been proved in space vehicles. Though the important material for the conventional solar cells is silicon, which is the
Chapter I Introduction: Amorphous semiconductors

second most abundant element in earth's crust, the major impediment is the expense in preparing high quality silicon in crystalline form. Amorphous or non-periodic solids form a class of materials with a greater diversity of physical properties. Their preparation usually does not require carefully controlled growth techniques, which is a vital economic advantage in many applications. Large number of methods is employed in the preparation of amorphous materials. These techniques are classified into two broad groups [National Academy of Sciences., 1972]. In the first category, a disorder in a material is introduced by thermal methods and the disorder contained in the liquid or vapor state is quenched sufficiently rapidly so that the attainment of internal configurational equilibrium is prevented leading to an amorphous material. In the second category of preparative techniques, the disorder is created in a solid below the temperature at which it can regain long range order in the time scale of the experiment. The rapid quenching of a melt as in melt quenching, melt spinning, splat cooling result in the formation of bulk glass. The vapor condensation like thermal evaporation, sputtering, glow discharge decomposition etc., in vacuum gives rise to amorphous films [Ovshinsky et al., 1978]. Once the amorphous solids/films are formed, it is confirmed by X-ray diffraction technique.

The mathematical complexity inherent in the non-periodic system inhibits a theoretical understanding of the microscopic properties of amorphous semiconductors, retarding their potential applications as electronic devices, though this complexity is now being reduced due to various models proposed.

The atomic forces which bind atoms in non-crystalline solids are analogous to those found in crystalline solids; the chemical bonding can be covalent, ionic, metallic, van der Waals or hydrogen bonding. Amorphous solids like crystalline solids can be insulators, semiconductors or metals and in some cases, at very low temperatures, they can even be superconductors, depending on the type of chemical bonding present in them.
Many terminologies are associated with non-crystalline solids such as non-periodic, disordered, amorphous, glassy etc., which can be treated as synonymous. The phrase "glass" is designated to the materials that exhibit the phenomena of "glass transition" on heating during which sudden changes are observed in thermal properties such as heat capacity, thermal expansion, etc [Turnbull, D., 1969; Owen, A.E., 1974; Bagley, A.G., 1975; Turnbull et al., 1975; Paul, A., 1982].

1.2.1 The Glass Transition

The phenomena of glass transition can be understood by considering a material that is being cooled from the melt. A liquid can solidify in two ways [Richard Zallen., 1983]: a) discontinuously to a crystalline solid or b) continuously to an amorphous solid (glass). Very often, cooling of a melt results in the crystallization of the material at the melting temperature $T_m$, where discontinuous changes occur (Fig. 1.1) in the first order thermodynamic parameters like volume, entropy and enthalpy [Kauzmann, W., 1948]. The crystalline solid thus formed has a long-range periodic order in its atomic arrangement. In certain cases the material in the molten state can be "supercooled" at temperatures below $T_m$, which becomes more viscous (of the order of $10^{13}$ poise) with the decrease in temperature (Fig. 1.1). As the supercooling is progressively continued, with the melt becoming more and more viscous, at a particular temperature, called the glass transition temperature $T_g$, the supercooled liquid freezes into a solid which is structurally rigid but possesses no long range order [Kauzmann, W., 1948]. In contrast to the crystallization of a melt, the liquid glass transformation is characterized by a gradual change in the first order thermodynamic parameters. However, sharp changes are exhibited in the second order thermodynamic parameters such as specific heat, compressibility, etc [Richard Zallen., 1983]. The typical variations in the thermodynamic parameters during crystallization and glass transition are shown in the figure 1.1.
Figure 1.1: Schematic illustration of the change in volume with temperature as a supercooled liquid is cooled through the glass transition temperature \((T_g)\). Paths 1 and 2 depict the fast and slow cooling rate of the melt. The first order phase transition accompanying crystallization from the melt is also shown.
Amorphous semiconductor falls into two broad categories Ge-type and Se-type. Table 1.1 consolidates some of their properties of these two types.

Table 1.1: Amorphous semiconductors

<table>
<thead>
<tr>
<th>Property</th>
<th>Ge-Type</th>
<th>Se-type</th>
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<tbody>
<tr>
<td>Coordination</td>
<td>4-fold:</td>
<td>2-fold:</td>
</tr>
<tr>
<td></td>
<td>Group IV and III-V semiconductors including Ge, Si and GaAs</td>
<td>Group IV chalcogenide alloys such as GeTe</td>
</tr>
<tr>
<td>Magnetic properties</td>
<td>Contain paramagnetic centers</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>Low temperature Conductivity</td>
<td>Exhibits hopping conduction</td>
<td>No evidence of hopping conduction</td>
</tr>
<tr>
<td>Dopability</td>
<td>Dopable after hydrogen passivation</td>
<td>Dopable by metallic additives</td>
</tr>
<tr>
<td>Application</td>
<td>Large area p-n devices of low cost</td>
<td>Optical memory devices and IR optical products</td>
</tr>
</tbody>
</table>

The bond structure of Ge-type amorphous semiconductors contains many localized deep lying mid-gap states caused by dangling bonds. These states are not present in Se-type Semiconductors. In both types of amorphous semiconductors, any dopant state near the top and bottom of the gap are not as extended as in crystalline semiconductors due to lack of long range order.

In tetragonally bonded Ge-type semiconductors such as amorphous silicon, the network is too stiff to allow much relaxation and consequently these materials retain a large number of localized mid-gap states. The paramagnetism of Ge-type amorphous
semiconductors is in fact due to unpaired electron spins in singly occupied mid-gap state. Such states also act as traps and recombination centers for charge carriers limiting the conductivity and thereby disallowing the possibility of doping. Although mid-gap states suppress conduction band conductivity, they provide an additional mechanism for conductivity not available in crystalline semiconductors known as the hopping conductivity. Hopping conductivity, the movement of electrons from one localized mid-gap state to another, actually dominates conduction band conductivity at room temperature in undoped Ge-type amorphous semiconductors. It is always desirable to eliminate such states in many types of tetragonally bonded amorphous semiconductors by the introduction of hydrogen to form Si-H bonds. Subsequent to such hydrogen passivation, doping of Ge-type amorphous semiconductors becomes possible. Hopping conductivity is absent in Se-type amorphous semiconductors due to lack of mid-gap states. The Ge-type is composed of predominantly Ge and Si prepared usually using vapor deposition techniques.

In Se-type amorphous semiconductors mid-gap states are swept away by the formation of bonds. Since Se-type amorphous semiconductors have only 2-fold coordination, the network is very flexible and can easily adjust itself to incorporate almost all of the dangling bonds into low energy bonding states in a process similar to surface reconstruction. The same process occurs when dopants are introduced. Dopant electrons are efficiently incorporated into bonds, effectively pinning the Fermi level at the mid-gap. As a result, Se-type amorphous semiconductors were believed to be not dopable. But recent studies have revealed that chemical modification is possible in Se-type amorphous semiconductors using metallic additives. The Se-type are those class of semiconductors containing at least one of the chalcogens S, Se or Te and can usually be prepared by conventional melt quenching. Many elements can combine with these chalcogens to form stable glasses exhibiting a variety of unique optical and electrical properties. Chalcogenide glasses are semiconductors with band gaps typically between 0.6 and ~1.4 eV. Use of chalcogenide glasses in p-n junction type devices has been hampered due to the inability to effectively dope the materials. The 2-fold coordination of chalcogenides as mentioned earlier, results in a very flexible network, which can easily
incorporate dopant electrons into low energy bonds. However recent work suggests that
certain chalcogenide glasses with higher coordination numbers may be an effective
customer to doping.

The potential application of chalcogenide glasses as electronic device was in the
field of electrophotography or xerography, where the photoconductive properties of
selenium–based glasses were exploited by the Xerox Corporation. In 1955, after the
discovery by Kolomiets [Kolomiets, B.T., 1964] and his co-workers that chalcogenide
glasses are semiconductors and many potential properties were studied. The most widely
exploited property of chalcogenide glasses is their large infrared transmittance in
combination with their chemical and mechanical durability. In comparison to other IR
optical materials such as fluoro zirconate glasses, which transmit only up to 7 micron,
chalcogenide glasses can transmit well beyond 10 microns. Although chloride, bromide
and iodide glasses transmit longer wavelengths than chalcogenides, the chemical and
mechanical durability of chalcogenide glasses have resulted in their wide spread use in
IR- optics and specialized fibre optic applications.

The most unique property of chalcogenides, however, is their ability to reversibly
switch from a resistive to a highly conductive state [Ovshinsky, S.R., 1968]. Large
reversible changes in optical characteristics are possible. Pioneering work in the area has
led to the development of chalcogenide-based memory devices such as "Phase-Change–
Erasable" (PCE) optical disks. Although chalcogenide glasses are semiconducting in the
amorphous phase, they can become highly conductive in the crystalline phase. Hence,
their electrical switching ability. Crystalline chalcogenides are much more reflective than
amorphous chalcogenides. The relatively low crystallization temp of 200°C combined
with the nearly crystalline structure of certain amorphous chalcogenides allow easy, very
rapid and reversible changes to and from fcc crystalline phase.

The unique bulk properties of chalcogenides become even more interesting when
they are in thin film form. Thin films are the key to exploiting the switching
characteristics of chalcogenides. Thin films allow current to flow through the highly
resistive amorphous state at relatively low voltages. It is believed that when a voltage is applied across a thin film, a current will flow in a conducting (albeit highly resistive) filament. At a critical threshold voltage, the ohmic power deposited into the filament is high enough to locally rise the temperature above crystallization value of \( \sim 200^\circ C \). (The filament proceeds to undergo a phase change to fcc and becomes highly conductive). This phase is stable which means that even if the voltage is brought to zero the filament remains conductive. The chalcogenide can be reversibly switched back to its highly resistive amorphous state by a quick current pulse that rises the temperature of the conductive filament above its melting temperature, generally \( \sim 500^\circ C \). If the pulse is short the chalcogenide is quickly quenched back into the amorphous state. A similar process is used when chalcogenide thin film is employed in phase change erasable optical disks. A single laser can be used to write, read and erase spots on the thin film depending upon the power and pulse length. This has seen applications in the field of computer storage in compact discs (CD-ROM, CD-R, CD-RW) and Digital Video Discs (DVD-ROM, DVD-RAM, DVD-RW).

1.3 Atomic Structure of Amorphous Semiconductors

The structural order in amorphous semiconductors can be classified depending upon the length scales [Elliott, S.R., 1991, Wright, A.C., et al, 1991, and Lucovsky, G., 1987] in which the local atomic species are arranged about a given reference atom. This classification is done for chalcogenide glasses due to the directional nature of the bonds.
### Table 1.2: Classification of structural order in amorphous semiconductors

<table>
<thead>
<tr>
<th>Short Range Order (SRO)</th>
<th>The short range order is associated with a length scale of 2-5 Å [Elliot, S.R., 1991].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Medium Range Order (MRO):</strong></td>
<td></td>
</tr>
<tr>
<td>Near MRO (NMRO)</td>
<td>The medium range order lie beyond the SRO with a length scale of 5-20 Å [Elliot, S.R., 1984, Elliot, S.R., 1991], which is further sub classified into three categories on the basis of increasing length scales as</td>
</tr>
<tr>
<td>Intermediate MRO (IMRO)</td>
<td>in the length scale of ~ 5 Å.</td>
</tr>
<tr>
<td>Far MRO (FMRO)</td>
<td>in the length scale of 5-8 Å.</td>
</tr>
<tr>
<td>Long Range Order</td>
<td>in the length scale of 8-20 Å.</td>
</tr>
<tr>
<td></td>
<td>absent in amorphous semiconductors.</td>
</tr>
</tbody>
</table>

The specification of the SRO include (a) the number of immediate neighbors, and their type, (b) their separation from the reference atom, and (c) their angular distribution. The specification of these aspects of the SRO does not completely determine the structure of the amorphous solids. A complete description of the structure requires a specification of the network topology that defines the way the atomic sites are interconnected with each other. For the covalently bonded amorphous semiconductors, the most important aspect of the overall topology relates to the distribution of the dihedral angles [Turnbull et al., 1972].

The two probes of the SRO is: (1) Radial Distribution Function (RDF's) derived by the traditional techniques of x-ray, neutron, and electron diffraction, and by a more recently developed technique based on EXAFS (Extended X-ray Absorption Fine Structure). (2) Analysis of vibrational spectra obtained by infrared absorption and reflection, and Raman scattering. The RDF techniques yield directly structural information, bond lengths, coordination numbers, etc., whereas the analysis of the IR and Raman spectroscopy yields information about bond types and the symmetries of the local atomic environments [Lucovsky et al., 1979].
A general empirical rule which governs the short-range order of amorphous semiconductors was first given by Ioffe and Regal [Ioffe, A.F and Regal, A.R., 1960] and is applicable to many materials. According to the Ioffe and Regal rule, the first coordination number of an amorphous semiconductor is the same as that in its crystalline counterpart. In other words, the nearest neighboring environment is the same in the amorphous and crystalline forms in many semiconducting materials, which is shown below.

![Figure 1.2: Comparison of radial distribution function of crystalline germanium and amorphous germanium.](image)

The x-ray derived RDF of amorphous Ge is shown in figure 1.2 in which the RDF of amorphous Ge is superimposed onto the crystalline Ge. The amorphous and crystalline comparisons were obtained under the same experimental conditions and using the same analytical transformation procedure [Temkin et al., 1973]. It is noticed from the
figure that in crystalline and amorphous Ge, the peak in RDF, corresponding to the first nearest neighbor distribution is almost the same in amorphous and crystalline phases of these materials. The RDF peaks of amorphous Ge broaden as the radial distance \( r \) increases. The absence of a peak in the vicinity of the crystalline third neighbor distance and the RDF converging into an asymptotic average density parabola at high values of \( r \) show the absence of long range periodic order.

1.4 Energy Band Structure of Non-Crystalline Semiconductors

The electrical properties of non-crystalline semiconductors can be understood by considering the energy band structure. In crystalline semiconductors, the electron density of states contains van Hove singularities and abrupt terminations at the valence band maximum and conduction band minimum. These sharp terminations at the edges in the density of states give rise to a well-defined forbidden energy gap. Within the band, the electron energy states are extended and occupy the entire volume. These features are the consequences of both the short-range and long-range structural 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. According to the tight binding picture of electrons, the available energy levels of an outer electron are estimated from the single atom levels, by perturbing them with the nearest neighbor interactions. As the nearest neighbor environments are the same in the crystalline and amorphous phases of semiconductors, the distribution of density of states is similar. The effect of disorder in electron distribution is to remove van Hove singularities and introduce band tailing [Frolich, H., 1947, Lifshitz, I.M., 1964, Gubanov, A.I., 1965].

localized in the sense that an electron in those regions will not diffuse at zero temperature to other regions. Since the localized and non-localized (extended) states cannot co-exist at the same energy, there is a sharp boundary (called the mobility edge), which separates the localized and extended states. The carrier mobility changes by a factor of 100, across the mobility edge.

There are several models proposed to explain the experimental observations, which are characteristics of most amorphous semiconducting materials.

1. Amorphous semiconductors are generally insensitive to doping. According to Mott [Mott, N.F., 1969] this is due to the satisfaction of normal valence requirements of the impurity atoms in an amorphous network.

2. The amorphous semiconductors are intrinsic-like with the Fermi level $E_F$ pinned near the midgap. This suggests that a high density of defect states exist [Mott, N. F., 1967] in the mobility gap.

1.4.1 Band Models

1.4.1.1 The Cohen-Fritzsche-Ovshinsky Model

The Cohen-Fritzsche-Ovshinsky (CFO) model [Cohen et al., 1969] assumes that the tail states extend across the gap in a structureless distribution. The gradual decrease of the localized states decreases the sharpness of the conduction and valence band edges. This extensive tailing of band edges implies that the conduction and valence band tails overlap, leaving an appreciable density of states in the middle of the gap as shown in the figure 1.3a. As a consequence, there are filled states in the valence band which have higher energies compared to the unfilled states in the conduction band. This results in a redistribution of the electrons forming negatively charged filled states in the conduction band and positively charged empty states in the valence band. This model therefore, ensures self-compensation, and pins the Fermi level close to the middle of the gap, as required by the experimental observations on the electrical properties of these materials [Fritzsche, H., 1973a; Fritzsche, H., 1974]. The localized tail states are separated from
the extended states in the band at critical energies called the mobility edges (E_C and E_V) as shown in the figure 1.3a. One of the major objections of the CFO model is the high transparency of the amorphous chalcogenides below a well-defined absorption edge [Mott, N.F and Davis, E.A., 1979]. It is evident from various experiments that the extent of band tailing in chalcogenides is rather limited to few tenths of an electron volt (eV) into the gap [Mott, N.F et al., 1979]. However, for amorphous Si, the CFO model may be more relevant [Nagels, P., 1979].

Figure 1.3: Schematic representation of the energy band structure of amorphous semiconductor. (a) The Cohen-Fritzsche-Ovshinsky (CFO) model. (b) The Davis-Mott model. (c) Modified Davis-Mott model.
1.4.1.2 The Davis-Mott Model

According to the Davis-Mott (DM) model [Mott et al., 1979; Davis et al., 1970; Mott, N.F., 1972], the structural disorder introduces "tailing" in the band edges, the tails of the localized states are narrow and extend to only a few tenths of an electron volt (eV) into the forbidden gap. This model based on several experimental results proposes a finite density of states at $E_F$ as shown in figure 1.3a. As long as the total density of states in the gap is not large, the model allows the observed transparency. The model proposes the existence of a band of compensated levels near the middle of the gap originating from the defects in the random networks (figure 1.3b). The defect states in the gap (dangling bond) act as both deep donors and acceptors with single and double occupancy conditions leading to the formation of two bands separated by an appropriate correlation energy or Hubbard $U$ (figure 1.3c). Based on this model, without additional compensating centres, $E_F$ should lie between the two bands or pinned between the bands.

If the model of gap states is adopted in which two bands of localized levels arising from defects overlap as in figure 1.3c, giving rise to a finite density of states at the Fermi level, one would expect an esr signal and Curie type paramagnetism to be exhibited by chalcogenide glasses. However, none of these phenomena are observed under normal conditions [Mott, N.F., 1985]. Though esr investigations by Agarwal [Agarwal, S.C., 1973] and Fritzsche [Fritzsche, H., 1973] showed signals only after heat treatment.

The contradicting fact that the absence of esr and paramagnetism with an essentially pinned Fermi energy was reconciled by Anderson [Anderson, P.W., 1975; 1976]. He suggested that the number of bonding situations available to the electrons in a glass is greater than the number of electron pairs, and that all orbitals are doubly occupied or empty. In other words, the electrons fill the states in pairs up to Fermi energy. According to this model, thermal excitation of single electron requires the effective
negative correlation energy $U_{\text{eff}}$ that is necessary to split the pairs. Thus a quasi-continuous distribution of energy levels provides explanation for pinning the Fermi level near the gap-center.

1.4.1.3 Emin's Small-Polaron Model

Emin (D. Emin, 1973; 1976a; 1976b) suggested that the electrical transport in amorphous chalcogenide glasses is of polaronic type of conduction. To understand this concept of polaronic conduction, consider an atomic lattice in which the atoms/ions are arranged in a regular pattern. An addition of a charge carrier into this lattice tends to displace the surrounding atom. If the charge carrier remains in the vicinity of a particular atomic site over a time interval long enough for the displacements of the surrounding atoms to take place due to the polarization of the surrounding lattice, a potential well may be created which can lead to trapping of the carrier. The unit built up by the trapped carrier and its induced lattice deformations is called a Polaron. If the carrier is confined to a single site, it is referred to as a small polaron. In its bound state, the carrier cannot move without the distortions of the neighboring atoms. The polaron has a lower energy than the free electrons but has a larger effective mass, since it must carry its induced deformation with it as it moves through the lattice. The presence of the disorder in a non-crystalline solid tends to slow down a carrier. This slowing down may lead to a localization of the carrier and, if the carrier stays long enough at an atomic site, it causes small polaron formation. Emin's small-polaron model was able to explain the experimental data of dc conductivity, thermopower and Hall mobility of some chalcogenide glasses.

1.5 Defects in Amorphous Semiconductors

The electrical transport properties of amorphous semiconductors are defect controlled [Elliott, S.R., 1984]. In many cases the behavior resulting from the presence of defects can completely dominate that due to the intrinsic material. In chalcogenide glasses, the ideal amorphous state is impossible to achieve experimentally since structural
defects are present even at thermal equilibrium in the melt and are consequently frozen-in on vitrification [Elliott, S.R., 1984].

When the co-ordination of any atom is less than optimal, the missing bonds are referred to as dangling. The energy of an atom with a single dangling bond is $E_b$ greater than that of the atom in its ground-state configuration, where $E_b$ is the bond strength. Since $E_b$ is typically about 2-6 eV, a dangling bond is energetically unfavorable [Ovshinsky et al., 1978]. Since the dangling bond states are localized, the unoccupied states are still higher in energy, on the average by the correlation energy, U [Hubbard, J., 1963].

**Figure 1.4:** (a) Schematic representation of the origin of valence and conduction band states for a tetrahedrally bonded semiconductor showing (i) atomic s and p-states (ii) sp$^3$- hybrid states, (iii) bonding ($\sigma$) and antibonding ($\sigma^*$) states (iv) broadening of ($\sigma$) 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.
The energy levels for electron states associated with an isolated dangling bond may be understood in terms of a simple molecular orbital picture. Considering the case of a tetrahedral semiconductor, say a-Si, having an atomic electronic configuration $s^2p^2$, the atomic levels hybridize to form four $sp^3$ molecular hybrids, each may admit a bonding or antibonding orbital, the molecular levels then broaden into bands owing to the solid-state interactions separated by a band gap (figure 1.4). A dangling bond containing a single electron will therefore have an energy level lying at the zero energy for the $sp^3$ hybrids, viz., near the middle of the gap (neglecting the atomic relations). Thus, structural defects such as dangling bonds are expected to introduce electron states deep into the gap, which is otherwise empty in the ideal case.

The density of states in the gap for an amorphous semiconductor containing isolated dangling bond defects is shown schematically in figure 1.4 [Elliott, S.R., 1984].

The bonding states ($\sigma$) are lowered in energy, while the antibonding orbital states ($\sigma'$) are raised in energy. The energy separation between the topmost filled band and the next higher empty band corresponds to the energy gap $E_g$. In Si, (figure 1.5a) the value of $E_g$ is $\approx 1.2$ eV, with the valence band being completely full while the conduction band being empty at $T = 0$ K. The band structures of amorphous phosphorus and amorphous Se atoms in their lowest energy configuration are shown in figure 1.5b and figure 1.5c respectively.

The difference in the band structures of amorphous P and amorphous Se compared to amorphous Si is that the former show no hybridization between $s$ and $p$ states (as in amorphous Si) which then split into bonding and antibonding states. One common feature observed in all the three classes of materials is that the conduction band is formed by antibonding orbital. The distinction between amorphous P and amorphous Se is in the valence band formation. According to Ovshinsky, [Ovshinsky, S.R., 1976a] the unique feature of chalcogen elements is the presence of the non-bonding $p$-orbital.
electrons (referred to as lone-pair electrons), which form the top of the valence band shown in figure 1.5.

**Figure 1.5:** Electronic structure of semiconductors is influenced by their bonding patterns. (a) In Si the configuration of lowest energy is attained when each atom is surrounded by a regular tetrahedron of other atoms. The s and p states hybridize and then split into bonding and antibonding states. (b) In phosphorus the configuration of lowest energy requires each atom to be bound to three nearest neighbors. Since the s and p states do not hybridize, each forms a filled energy band in the solid.
Figure 1.5: contd... (c) In selenium atom, when selenium bonds with two of its neighbors, the atom is in the lowest energy configuration as shown above. The optimum bond angle is between 100 and 105 degrees.

1.5.1 Charged Dangling Bond Model

The transport properties of amorphous semiconductors are controlled by the intrinsic defects which exist in the gap states. Since these defects have low creation energy, they can be present in sufficiently large concentrations and control the transport behavior [Mott et al., 1979]. The defects in crystalline semiconductors are known. In amorphous materials due to the non-periodicity in their structures the defects can exhibit over a much wider range.
Chapter 1

Introduction: Band models

Street and Mott [Street and Mott., 1975] and Mott et al., [Mott et al., 1975a] first proposed the importance of discrete dangling bond defects at which electrons experience negative effective correlation energy and later by Kastner et al., [Kastner et al., 1976].

1.5.2 Street and Mott Model

According to Street and Mott [Street, R.A and Mott, N.F., 1975] the localized gap states are constituted by randomly distributed dangling bonds with concentrations of $10^{18} - 10^{19}$ cm$^{-3}$ for glassy Se with the density of chalcogen atoms $\sim 10^{22}$ cm$^{-3}$ and $T_e \sim 300K$. The essential features of the charged dangling bond can be understood by considering the monatomic amorphous Se system. The structure of amorphous Se, which is two fold coordinated, (three for As), is believed to consist mainly of chains (with few rings). Any chain end will be the site of dangling bond orbital which in the simplest case will contain an unpaired electron and be electrically neutral relative to the bulk. Mott et al., [Mott et al., 1975a] referred to this dangling bond defect as $D^0$, where the superscript indicates the charge state. In other words, the dangling bonds $D^0$ are point defects at which the normal coordination cannot be satisfied because of the constraints due to local topography. They postulated following Anderson [Anderson, P.W., 1975] that electrons residing at $D^0$ centres should experience a negative $U_{eff}$ and electron pairing should be energetically favorable due to atomic rearrangements. In amorphous chalcogenides, electron-lattice distortion is strong due to the low atomic coordination which results in a high degree of network flexibility. The existence of non-bonding lone-pair orbital at the chalcogen atoms favors additional bond formation which are energetically favorable since they form the top of the valence band [Kastner, M., 1972]. The transfer of an electron, from one $D^0$ centre to another produces one site, which has the original dangling bond orbital containing two spin-paired electrons and which is consequently negatively charged ($D^-$), and the other which has an empty orbital which is then free to form a dative bond with the lone-pair of a fully connected neighboring atom; the defect now becomes three-fold coordinated and positively charged ($D^+$). The reaction is assumed to be

$$2D^0 \rightarrow D^+ + D^- \quad (1.1)$$
The above reaction is exothermic, that is the total energy (electron + lattice) associated with the pair of charged defects $D^+$ and $D^-$ (both without spin) is lower than that of two neutral defects $D^0$ (both with spin). The most important aspect of the above equation is that it is exothermic due to the effective negative correlation energy $U_{\text{eff}}$. The energy gained due to the extra bond formation more than compensates for the coulomb repulsion resulting from the addition of an electron to the other dangling bond [Street et al., 1975]. This process is thus treated in terms of a configurational coordinate diagram (figure 1.6).

![Configuration-coordinate diagram](image)

**Figure 1.6**: Configuration-coordinate diagram for the formation of a $D^+$-$D^-$ pair. Exchange of an electron between two $D^0$ centres to $D^+\cdot D^-$ pair at the same configuration requires an energy $U$. The $D^+\cdot D^-$ centres subsequently relax to a different configuration with the overall energy being lowered by the effective correlation energy $U_{\text{eff}}$.

Though this model is highly successful in explaining many experimental results, it has certain limitations. The main objection is the assumption of high density of dangling bonds [Kastner, M and Fritzsche, H., 1978]. Also, it does not explain why a large negative $U_{\text{eff}}$ characterizes amorphous materials.
1.5.3 Kastner Adler Fritzsche Model

The normal chemical bonding in chalcogenide materials is quite different from that in tetrahedral materials whether amorphous or crystalline [Kastner, M., 1972]. Ovshinsky and co-workers [Ovshinsky, S.R., 1976b] explained that these differences in bonding together with the absence of steric constraints might, in the amorphous phase lead to unusual coordination numbers. Thus development of a chemical bond approach culminated in 1976 with the valence-alternation (VA) model of Kastner, et al. [Kastner et al., 1976]

According to Kastner Adler Fritzsche (KAF) model, [Kastner et al., 1976] only those defects, which are thermodynamically favorable, will be present in the glass. This is because point defects require only a finite free energy, \( G_f \) for creation. So if there are \( N_0 \) sites in the solid, then the number of defects in the solid

\[
N = N_0 \exp \left(-\frac{G_f}{kT}\right)
\]  

In a glass, the lowest temperature at which the defects anneal away is the glass transition temperature, \( T_g \). The density of defects is thus determined by \( T_g \) and free energy of creation of the defects \( (G_f) \).

Ovshinsky [Ovshinsky, S.R., 1975] suggested that interactions between lone-pair electrons [Kastner, M., 1972] on different atoms, and interactions with their local environment result in localized states in the gap of chalcogenide glasses. The specific interactions between nonbonding orbital give rise to unusual bonding configurations called as Valence alternation pairs (VAPs). These configurations result, for example, when two chalcogen atoms, each two fold coordinated in its ground state, form one positively charged three fold coordinated atom and one negatively charged singly coordinated atom.
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Figure 1.7: The Kastner-Adler-Fritzsche model of defects in chalcogenide glasses. The arrows represent electrons with spin. Energies are represented with the lone pair energy as zero. An electron in a σ state is always paired with one from a nearest neighbor atom as shown.

The energy required for the creation of VAP is relatively small, hence the density of VAPs in most glasses is relatively large.
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\[ 2C_2^0 \rightarrow C_1^+ + C_1^- \]  
\hfill (1.3)

which costs energy

\[ -3E_b - E_b + U_\text{LP} + 4E_b = U_\text{LP} \]  
\hfill (1.4)

where \( U_\text{LP} \) is the electronic correlation energy in the non-bonding states. \( C_1^0 \), the dangling bond [Street et al., 1975] costs full energy \( E_b \) and is energetically unfavorable. \( C_3^0 \) is the lowest energy neutral defect (figure 1.7). However, KAF have shown that \( C_3^0 \) is unstable and thus the first charge transfer reaction yields \( C_3^+ \) and \( C_3^- \) as under

\[ 2C_3^0 \rightarrow C_3^+ + C_3^- \]  
\hfill (1.5)

which costs an energy

\[ -3E_b - E_b + 2\Delta + U_{\sigma^*} + 4E_b - 2\Delta = U_{\sigma^*} \]

This reaction costs energy \( U_{\sigma^*} \). This positive correlation energy term \( U_{\sigma^*} \) arises because two electrons are in the antibonding state near the \( C_3^- \). Simply by breaking one of the three bonds \( C_3^- \) spontaneously becomes an ordinary \( C_2^0 \) converting a nearest neighbor \( C_2^0 \) site into a singly coordinated chalcogen with the extra electron, \( C_1^- \) according to the reaction

\[ C_1^- + C_2^0 \rightarrow C_2^0 + C_1^- \]  
\hfill (1.6)

the above reaction costs an energy as given below and is exothermic if

\[ -E_b + 2\Delta + U_{\sigma^*} - 2E_b + 2E_b + E_b - U_\text{LP} > 0 \]

this implies

\[ 2\Delta = (U_\text{LP} - U_{\sigma^*}) > 0 \]

The system can thus lower its energy by transferring two \( \sigma \) and two \( \sigma^* \) electrons into the lone pair states of one singly coordinated and one two-fold coordinated chalcogen. The reaction thus yields to

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

Kastner et al. 1976, (KAF model) showed that the lowest energy neutral defect in an amorphous chalcogenide is not a dangling bond i.e., a singly coordinated chalcogen atom viz., \( C_1^0 \) but rather a three fold coordinated chalcogen atom, \( C_3^0 \). The former \( C_1^0 \) costs
bond energy, $E_b$, while the latter only costs the excess antibonding repulsive energy, $\Delta$. However, Vanderbilt and Joannopoulos [Vanderbilt et al., 1979] suggest that the singly coordinated neutral defect is the least energy defect.

Further, since positively and negatively charged centers attract one another via the coulomb interaction, the defect centers with oppositely charged chalcogens as nearest neighbors have the lowest energy of all. These nearest neighboring pairs are called intimate valence alternation pairs (IVAPs). Non intimate pairs (NVAPs) are also possible, but they will have energies greater then IVAPs [Adler et al., 1977].

1.6 Electrical Properties of Chalcogenide Glasses

The Davis-Mott model forms the starting point to describe the transport properties of amorphous semiconductors.

1.6.1 dc Electrical Conductivity

The major distinguishing feature of an amorphous semiconductor as suggested by Davis-Mott model is the existence of narrow tails of localized states at the extremities of the valence and conduction bands. Further, a band of localized levels, within the mobility gap can be divided into two parts:
(a) Inherent states due to the disorder that leads to band tails;
(b) Point defects that lead to a midgap density of states (DOS).
Consequently, the density of states can be depicted as shown in figure 1.8. The conduction band edge $E_C$ separates localized states from those that are extended. Hence, the transport processes can be divided into several categories leading to different channels for conduction, namely;
(i) Extended state conduction   (ii) Conduction in band tails and
(iii) Conduction in localized states at the Fermi energy.
Figure 1.8: Density of states (DOS) diagram for a-Si alloys showing the distinction between tail states and deep defect states. a, b, c, and d represent the expected conduction mechanisms for electrons (Arun Madan and Melvin P. Shaw., 1988).

1.6.1.1 Conductivity in Extended States.

Extended state transport occurs via carriers excited beyond the mobility edge into states at or above \( E_C \) (or below \( E_V \)), as shown in figure 1.8. Since the conduction is expected to occur within about \( kT \) of the edge at \( E = E_C \), then the conductivity for n-type conduction can be expressed as

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

(1.7)

where the pre-exponential factor \( \sigma_0 \) is given by
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\[ \sigma_e = eN(E_c)kT\mu_c \]  

(1.8)

where \( N(E_c) \) is the density of states at the mobility edge \( E_c \) and \( \mu_c \) is the mobility. Electrons at and above \( E_c \) can move freely while those below it can move only through activated hopping (Nagels, P., 1979) and the conductivity mobility is given by

\[ \mu_c = \frac{2\pi a^2}{3h} Z \left[ \frac{J}{kT} a^3 J N(E_c) \right] \]  

(1.9)

where \( a \) is the interatomic spacing, \( Z \) the coordination number, and \( J \) the electronic transfer integral. The carrier mobility decreases with increasing temperature. The variation in dc electrical conductivity with temperature as expected from the Davis-Mott model is shown in figure 1.9 in which the region 'a' corresponds to the conductivity in extended states, by carriers beyond the mobility edge. The carrier mobility in region 'a' is found to be of the order of 2 cm\(^2\) V\(^{-1}\) s\(^{-1}\) (Nagels P, 1979).

1.6.1.2 Conductivity in the Tail States

The conductivity in the tail states occurs by thermally activated hopping with charge transport from one localized state to another with an exchange of energy with a phonon.

\[ \log \sigma_{dc} \] versus \( 1/T \) corresponding to the conduction mechanism (Davis and Mott., 1970).
Figure 1.10: Density of states in the Anderson model when states are non-localized in the center of the band. Localized states are shown shaded, $E_C$, $E_C'$ separate the ranges of energy where states are localized and non-localized (Mott. N.F and Davis, E.A, 1979).

The tail states shown in figure 1.10 generated by disorder, lie in the energy ranges $E_A < E < E_C$ and $E_V < E < E_B$, for the conduction and valence bands respectively. The conduction at an arbitrary energy $E = E_X (E_A)$ in the tail states, shown by path (b) in figure 1.8 is given by

$$
\sigma = \sigma_{\text{hop}} C_1 \exp \left[ - \left( \frac{E_A - E_V + W_t}{kT} \right) \right] \quad (1.10)
$$

where $W_t$ is the energy difference between the states (hopping energy). In the expression (1.10), $\sigma_{\text{hop}}$ is given by the relation

$$
\sigma_{\text{hop}} = \left( \frac{1}{6} \right) v \rho e^2 R^2 N(E_C) \quad (1.11)
$$
and

\[ C_i = 1 - \exp \left( \frac{-\Delta E}{kT} \right) \left[ 1 + \left( \frac{\Delta E}{kT} \right) \right] \]  

(1.12)

In the above expressions, \( v_{ph} \) is the phonon frequency, \( R \) is the hopping distance and \( \Delta E = E_C - E_A \).

The thermally activated mobility is given by

\[ \mu_{\text{hop}} = \mu_o \exp \left( -\frac{W_1}{kT} \right) \]  

(1.13)

and the pre-exponential factor \( \mu_o \) has the form

\[ \mu_o = \left( \frac{1}{6} \right) v_{ph} \frac{eR^2}{kT} \]  

(1.14)

From figure 1.9, the region ‘b’ corresponds to the conduction in the band tails, the carrier mobility in the region ‘b’ is of the order of \( 10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) for a typical phonon frequency \( v_{ph} = 10^{13} \text{ s}^{-1} \) and \( W_1 \sim kT \) (Nagels P, 1979).

1.6.1.3 Conduction in Localized States at The Fermi Energy

As predicted by Davis-Mott model, if the Fermi energy lies in a band of localized states; the charge carriers can move between the states via a phonon-assisted tunnelling process which is analogous to impurity conduction observed in heavily doped and highly compensated semiconductors at low temperatures. The hopping of carriers between localized states situated in the mid-gap region \( (E_A < E < E_B) \) occurs either at low temperatures, or high temperatures in materials with a high defect state density, this is shown by path ‘c’ for electrons in figure 1.8. The probability that a carrier jumps from one localized state to another state of higher energy will depend upon:

(a) \( \exp [-W_2 / kT] \), where \( W_2 \) is the energy difference between the two states;
(b) \( v_{ph} \), the phonon spectra; (in the range \( 10^{12} - 10^{13} \text{ s}^{-1} \) )
(c) \( \exp [-2 \alpha_L R] \); the overlap of the wave functions where \( R \) is the distance separating the two localized states and \( \alpha_L \) is the decay factor.
Considering only the electrons at $E_F$, for weak fields the conductivity is given by [Mott et al., 1979]

$$\sigma = \sigma_0 \exp \left[-\frac{W_1}{kT}\right]$$  \hspace{1cm} (1.15)

where

$$\sigma_0 = \left(\frac{1}{6}\right) e^2 R^2 v_0 N(E_F) \exp (-2\alpha_s R)$$  \hspace{1cm} (1.16)

In figure 1.9., the region 'c' corresponds to the conduction in localized states at the Fermi energy according to equation (1.15).

For strong localization ($\alpha_s R >> 1$) nearest neighbor hopping is to be expected.

However, in the weak localization case, the electrons will have a wider choice of centers to hop to and the material exhibits variable range hopping [Mott, N.F., 1968]. In this case the hopping distance $R$ increases with decreasing temperature since the electrons will have a higher probability of jumping to a more distant site where $W_2$ is smaller. By maximizing this probability, it can be shown that the conductivity is given by

$$\sigma = \sigma_0 \left(T\right) \exp \left(-\frac{B}{T^{1/4}}\right)$$  \hspace{1cm} (1.17)

$$B = 2.1 \left[\frac{\alpha^2}{kN(E_F)}\right]^{1/4}$$

Equation (1.17) is Mott's $T^{1/4}$ Law, which is applicable for transport in the three dimensional case. For transport in two-dimensional case [Mott et al., 1975b], equation (1.17) leads to

$$\sigma \propto T^{-\frac{1}{2}}$$  \hspace{1cm} (1.18)
This theory implies the change from $T^{-1/2}$ to $T^{-1/4}$ behavior as the sample thickness is increased.


1.6.2 Thermopower

Thermo-electric power (or thermopower) is another transport property closely related to $\sigma$ which gives a great deal of information about transport mechanisms in amorphous semiconductors. The thermopower, $S$ may be written as [Mott et al., 1979]

$$S = -\frac{k}{<e>} \int \sigma_g \frac{(E - E_g) \partial f(E)}{kT} \partial E dE$$

where $<e>$ is the value of the electronic charge and

$$\sigma_g = eN(E)\mu(E)kT$$

1.6.2.1 Conduction in Extended States

For the case of band conduction of electrons in the extended states assuming a constant density of states, i.e., $N(E)$ and $\mu(E)$ are constant the thermoelectric power is given by

$$S_{\text{ext}} = -\frac{k}{e} \left( \frac{E_c - E_F}{kT} + A \right)$$
where $kT$ is the average energy of the transported electrons with respect to $E_c$; for amorphous semiconductors, and conduction in extended state, $A = 1$. If $(E_c - E_p)$ is temperature dependent, then

$$S_{ext} = - \frac{k}{<e>} \left( \frac{\Delta E_g}{kT} - \frac{\gamma}{k} + 1 \right)$$  \hspace{1cm} (1.21)$$

it is apparent that the slopes of the curves $\ln \sigma$ versus $1/T$ and $S$ versus $1/T$ should be the same if conduction is in extended states. Measurements of thermopower can be used to obtain the value of $\gamma$, the temperature coefficient of $(E_c - E_p)$, from the intercept of $S$ versus $1/T$.

### 1.6.2.2 Conduction in Localized States Near The Mobility Edge

The thermopower also results if current is carried by carriers hopping between localized tail states. If the density of states in this region is assumed to vary as $N(E)$ proportional to $(E - E_A)^8$, the thermopower takes the form

$$S = - \frac{k}{<e>} \left( \frac{E_A - E_F}{kT} + K \right)$$  \hspace{1cm} (1.22)$$

where $K$ is a constant different from $A$ in equation (1.20).

If the carriers move by hopping in the localized states, the conductivity varies nearly exponentially with temperature, and the measured activation energy is the sum of the activation energies for carrier creation and for hopping. The activation energy for hopping does not appear in the expression for $S$, and, therefore, a difference in slope results between the conductivity and thermopower curve.
1.6.2.3 Conduction in Localized States at the Fermi Energy

At low temperature, charge transport arises from electrons tunneling between states at $E_F$. According to Cutler and Mott [Cutler and Mott, 1969] the thermopower should be identical to the equation used for metallic conduction. Hence

$$S = \frac{n^2 k^2 T}{3e} \left[ \frac{d \ln \sigma(E)}{dE} \right]_{E_F}$$  \hspace{1cm} (1.23)

since the Fermi level lies in a region where the density of states is finite, the thermopower will be small. Its sign may be positive or negative depending on whether the major contribution to the current is below or above the Fermi energy.

1.6.3 Hall Effect

In crystalline semiconductors, for unipolar conduction, the measurement of Hall coefficient $R_H$ provides an estimate of the charge carrier concentration $n$ and the carrier type.

In amorphous semiconductors the mobility is very low, and the carriers move with a mean free path, which is very short and is comparable to the interatomic distance and the scattering is very strong. It is found that in all the amorphous semiconductors, the sign of $R_H$ is always opposite to that of thermopower [Elliott, S.R., 1984; Yoffa et al., 1977; LeComber et al., 1977]. Using the Random phase model [Friedman, L., 1971], Friedman was able to find an expression for the Hall mobility which is applicable to the conduction regime in the extended states near the mobility edge and is given by the relation

$$\mu_H \equiv 2\pi \left( \frac{e \alpha^2}{h} \right) \left( \frac{B_0}{B} \right) \frac{\eta Z}{Z^2}$$  \hspace{1cm} (1.24a)
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Here $B_0$ is the bandwidth in the absence of disorder ($= 2ZJ$), where $Z$ is the coordination number and $J$ the overlap integral, $B$ is the bandwidth with disorder ($= [a^3 N(E_C)^{-1}]$), $Z$ is the number of interacting sites and a minimum of three sites is necessary in order to obtain a Hall effect; and $\eta$ is the projection of the area of a three-site path in the direction perpendicular to the field ($= 1/3$ for 3-D). Substituting all these factors equation (1.24a) becomes,

$$\mu_H \equiv \frac{4\pi ea^3}{3} J N(E_C) \left( \frac{Z}{Z} \right)$$ (1.24b)

From the above equation it follows that the Hall mobility within the random phase model is independent of temperature in contrast to the conductivity mobility $\mu_c \propto 1/T$ [Emin, D., 1976a]. The magnitude of $\mu_H$ as obtained by Friedmann was found to be $\equiv 10^{-1} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ against $\mu_c \equiv 10 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. The Hall mobility is related to the conductivity mobility by a simple relation

$$\frac{\mu_H}{\mu_c} \equiv \frac{2kT}{Z J}$$ (1.25)

where generally $J > kT$ ($J \equiv 1 \text{eV}$). The main feature resulting from Friedman’s treatment is connected with the sign of the Hall coefficient. For a configuration of three interacting sites the Hall coefficient is negative, even if holes are responsible for the conductivity. This result is consistent with the p-n anomaly between the thermopower and the Hall effect commonly encountered in amorphous semiconductors [Friedman, L., 1971; Holstein, T., 1973].

1.6.4 Photoconductivity

The conductivity in the presence of photoexcitation $\sigma_L$ is given by

$$\sigma_L = (n e\mu_n + n_0 e\mu_n) + (p e\mu_p + p_0 e\mu_p)$$ (1.26)
where \( n \) and \( p \) are the electron and hole carrier concentrations due to optical excitation, \( n_0 \) and \( p_0 \) the thermal equilibrium concentrations in the dark and \( \mu_n \) and \( \mu_p \) the conductivity mobilities of electrons and holes. The photoconductivity, \( \sigma_{ph} \) is defined as

\[
\sigma_{ph} = \sigma_L - \sigma_D
\]

(1.27)

The study of photoconductivity characteristics of a semiconducting material can be conveniently expressed in terms of the number of free carriers, example, electrons as

\[
n = G\tau_n
\]

(1.28)

where \( G \) is the volume generation rate and \( \tau_n \) is the life time of the free carriers.

Photoconductors in general exhibit

\[
\sigma_{ph} \propto G^\gamma
\]

where \( \gamma \) can be unity, greater than unity, less than unity, or equal to 0.5 [Albert Rose., 1960]. All of these characteristics were exhibited by amorphous silicon. [Anderson et al., 1977; Zanzuchi et al., 1977; Vanier et al., 1981; and particularly by Wronski and Daniel, 1981]. Because of the continuous distribution of states in amorphous semiconductors, the occupancy of states of the recombination centers will depend on the level of photoexcitation. This leads to a non-linear dependence of \( \sigma_{ph} \) on the generation rate \( G \), and is represented by

\[
\sigma_{ph} \propto G^\gamma
\]

(1.29)

the value of \( \gamma \) depend on the distribution of states. The density of trapped electrons within the semiconductors is given by,

\[
n_t(E) = N_t(E)\exp\left(\frac{(E_f - E_{ph})}{kT}\right)
\]

(1.30)

where \( E_{ph} \) is the quasi-Fermi energy, due to a non-equilibrium situation.
It should be recognized that the shallow trapped electrons do not directly influence the recombination mechanism. However, the transient response is affected by these states since the onset of the termination of illumination involves not only the return of the free electrons to thermal equilibrium, but also the return of all the trapped carriers. If the recombination rate \( (n/\tau_n) \) is less than the emission rate, the time taken to decay to half its value, \( \tau_0 \), is given by

\[
\tau_0 = \left(1 + \frac{\tau_n}{n}\right) \tau_n \tag{1.31}
\]

1.7 Electrical Switching in Amorphous Semiconductors

The application of high electric fields (\(~10^6\) V/cm) to certain solids leads to a nonlinear electrical characteristics [Dewald et al., 1962; Ovshinsky, S.R., 1968]. In insulating materials, such high fields lead to a destructive breakdown owing to the space-charge effects, ion drift and the large bandgap of these materials, which limit the reproducibility [Chopra, K.L., 1970 and Dearnaley et al., 1970]. A number of crystalline and amorphous semiconductors are found to exhibit switching and negative resistance phenomena at higher fields. The negative resistance effects observed in the materials can be generally classified into six possible types (figure 1.11).

1.7.1 Voltage Controlled Negative Resistance (VCNR)

A material exhibiting VCNR shows a ohmic behavior, starting from a low resistance, up to a critical voltage \( V_c \). Above \( V_c \), the material passes through a negative resistance region to reach a high resistance state. The I-V characteristic is retraced, when the voltage is reduced as shown in figure 1.11a. [David Adler., 1971; Fritzsche, H., 1974].
In a VCNR device with memory (figure 1.11b), once the high resistance state is reached, it is retained even after the reduction of the field. Amorphous oxides like Al$_2$O$_3$, Ta$_2$O$_5$, ZrO$_2$, etc., exhibit VCNR and VCNR with memory [David Adler, 1971; Fritzche, H., 1974].

![Graph of six types of non-ohmic behavior observed in amorphous materials.](image)

**Figure 1.11:** Six 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 (David Adler, 1971).

### 1.7.2 Current Controlled Negative Resistance (CCNR)

In a CCNR device the voltage increases with current initially. At a threshold current $I_t$ (corresponding to threshold voltage $V_t$), the voltage starts decreasing with increasing current, passing through a negative resistance zone, to a low resistance state. If the current is reduced, the characteristic is retraced as shown in figure 1.11c.
In a CCNR with memory, the low resistance state once set, is retained even under zero-bias condition. Hence, this is a bi-stable device under zero bias condition (figure 1.11d). CCNR behavior with and without memory effects, is observed in materials like MoO$_3$, NbO$_5$ etc., [David Adler., 1971; Fritzsche, H., 1974].

1.7.3 Switching

The characteristic of a 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 indicated in the figure 1.11e and 1.11f. At the threshold current $I_t$ (corresponding to voltage $V_t$), the device switches to the low resistance state in a very short time (<10$^{-10}$ s) [Fritzsche, H., 1974].

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 conducting state cannot be maintained and the device switches back to the high resistance OFF state retracing the original path. In contrast, the memory switching devices when once switched retains its conductive low resistance ON state even when the current approaches and reaches zero (figure 1.11f) [Fritzsche, H., 1974]. Threshold and memory switching has been observed in a variety of crystalline and amorphous materials, such as Nb$_2$O$_5$, CdCr$_2$Se$_4$ etc., [Hiatt et al., 1965; Herrell, et al., 1972; Roy et al., 1969; Tanaka et al., 1970; Uttechi, et al., 1970].

Electrical switching in amorphous semiconductors was first observed by Ovshinsky [Ovshinsky, S.R., 1968]. Studies on bulk and thin films of chalcogenide glasses have shown electrical switching exhibited by these samples.

In threshold switching glassy thin film materials [Adler et al., 1980], the particularly desirable characteristics in multicomponent amorphous chalcogenide is clear due to the following: (i) the high resistivity of the OFF-state resulting from the trap-limited mobility inhibits joule-heating effects. (ii) the nearly equal densities of positively
and negatively charged traps inhibit large ON state bulk space charge effects. (iii) the presence of large concentrations of cross-linking atoms inhibits crystallization and (iv) the fact that the valence electrons are nonbonding allows for the excitation of large free-carrier concentrations without decrease in structural stability. Switching behavior has been reported on many ternary and quaternary chalcogenide systems like Ge-As-Te and Ge-As-Se thin films [Pinto, R., 1971], bulk As$_{16}$Ge$_{15}$Te$_{75}$ [Vohra et al., 1990], Cd-Ge-As$_2$ bulk samples [Kug Sun Hong et al., 1990] Al$_{10}$As$_7$Te$_{90-x}$ (20 ≤ x ≤ 40) and Al$_{20}$As$_7$Te$_{90-y}$ (10 ≤ y ≤ 40) [Algeria et al., 1983], Te$_{46}$As$_{30}$Si$_{12}$Ge$_{10}$ using planar electrode configurations with inter electrode spacing ~1 micron [Armitage et al., 1970], etc., to mention a few. Studies on binary system, viz., Ge$_{20}$Te$_{100-x}$ (12 ≤ x ≤ 25) was undertaken by Nagaraja Murthy, C [Nagaraja Murthy, C., 1999]. It was reported that the sample exhibited current controlled negative resistance behavior with memory. It was also reported that these samples exhibited marginal threshold behavior while decreasing the current in the ON-state. Here, while the samples Ge$_{15}$Te$_{85}$, Ge$_{17}$Te$_{83}$ and Ge$_{20}$Te$_{80}$ exhibited a threshold tendency, Ge$_{23}$Te$_{77}$ and Ge$_{25}$Te$_{75}$ showed pure memory behavior. Similar marginal threshold behavior is noticed in Si$_x$Te$_{100-x}$ (15 ≤ x ≤ 25). The quaternary system like Si-Te-As-Ge (STAG) [Ovshinsky, S.R., 1968] has been found to exhibit threshold switching. However, the threshold behavior is limited to a narrow composition range, while the other compositions of the series lead to memory switching behavior.

1.7.4 Parameters of Electrical Switching

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Earlier studies on other types of non-oxide glasses such as As glasses and amorphous Ge and Si [Fulenwider et al., 1970] showed switching and memory effects but none with the reliability and stability as that of chalcogenide glasses. In chalcogenide glasses, the switching process occurs when the voltage drop across the sample exceeds a threshold voltage $V_t$, wherein the resistivity of the sample changes. Once the switching has commenced it proceeds very rapidly within a switching time $t_s \leq 10^{-10}$ sec [Ovshinsky et al., 1973] along the load line to the conducting branch of the characteristic. The switching mechanism in chalcogenide glasses can be understood by the following device parameters.

1.7.4.1 Switching Voltage ($V_t$)

When a voltage exceeding the threshold voltage ($V_t$) is applied, the material switches to the conducting state along the load line. The threshold voltage depends on the thickness of the sample, electrode separation, ambient temperature and the nature of excitation (viz., DC, pulse, ramp, etc.). It is therefore essential to specify the conditions under which $V_t$ is measured.

1.7.4.2 Delay Time ($t_D$)

The switching material does not switch immediately to the conducting state as the threshold voltage is increased. The material remains in the high resistance state for a period of time known as the delay time ($t_D$). The time interval between the application of voltage pulse $V_p$ and the initiation of the actual switching process is called the delay time ($t_D$) (figure 1.12a).
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Figure 1.12: Time response of voltage pulse $V_p > V_t$ for (a) a threshold switch and (b) a memory switch. Switching from OFF to ON occurs after a delay time $t_D$. The memory is set after a lock-on time interval $t_{LO}$ after switching. The threshold switch (a) returns to OFF at the end of the $V_p$ pulse. The memory switch (b) requires a RESET current pulse to return to a high resistance state.

The delay time is typically of the order of $10 \mu$ sec for a threshold device [Fritzsche, H., 1974; Ovshinsky et al., 1973]. The delay time decreases rapidly as $V_p$ is increased beyond $V_t$, and for $V_p > 1.2 V_t$ it follows the relation [Ovshinsky, S.R., 1968; Henisch, H.K., 1969; Shanks, R.R., 1970; Lee and Henisch., 1973; Bunton et al., 1971; Bunton et al., 1973].

$$t_D = t_{DO} \exp \left[ - \alpha V_p \right]$$

The prefactor $t_{DO}$ decreases with increasing ambient temperature [Boer et al., 1970] and decreasing electrode separation. Figure 1.13 shows that the delay time decreases exponentially with over voltage [Bunton et al., 1973] and attains values of the order of $10^{-9}$ sec at applied voltages of about 50% higher than the threshold voltage [Ovshinsky et al., 1973; Fritzsche, H., 1973a]. When the over voltages are less than 20% of $V_t$,
the fluctuations in the delay time are observed typically from $10^{-6}$ sec to $10^{9}$ sec [Fritzsche, H., 1973a, p 562]. These fluctuations in delay time $t_D$ are of no consequence because digital devices are operated with sufficient over voltages to increase the speed.

1.7.4.3 Switching Time ($t_s$)

In both threshold and memory switching, once the switching is initiated, the material changes its state very rapidly within a time known as the switching time of the device and is given by $t_s \leq 10^{-10}$ sec [Fritzsche, H., 1973]

1.7.4.4 Lock-on Time ($t_{LO}$)

The Lock-on time refers to memory switching. When a memory material switches to the low resistance state, after the delay time $t_D$, then the memory switch retains its conductive state only after it has been kept in this state for a minimum period of time known as the Lock-on time $t_{LO}$. In this time $t_{LO}$, the material is said to set in the memory state [Ovshinsky et al., 1973; Owen et al., 1973; Warren, A.C., 1973]. If the set voltage pulse $V_p$ is less than $t_D + t_{LO}$, then the memory switch reverts back to its high resistance state as shown in figure 1.12b. The Lock-on time is typically found to be higher than 100μ sec [Bunton et al., 1973].

1.7.4.5 Recovery Time ($t_R$)

In a threshold switch, after the sample is switched, a definite time is required by the sample to recover to its original state, while the sample is being brought back to the initial high resistance state by reducing the current below $I_h$. This time is

![Figure 1.14: Typical recovery curve of threshold switch after switching process (Morin, F.J., 1959; Henish and Pryor, 1971).]
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 at a lesser voltage $V_t$ [Fritzsche, H., 1973; Fritzsche, H., 1974; Owen et al., 1973 p 140; Warren, A.C., 1973, p 105]. Figure 1.14 shows the recovery curve of a threshold voltage after the switching process. The dependence of the threshold voltage on the time interval between two successive voltage pulses is clearly depicted [Henisch et al., 1971].

1.7.4.6 Set ($t_{SET}$) and Reset ($t_R$) Time of Memory device

Set time $t_{SET}$ is applicable to the memory device and is the time required to "Set" the device from the high resistance OFF state to the low resistance ON state. It is of the order of milli sec of the lock-on time [Fritzsche, H., 1974], to set the device into memory state. The set time is the sum of $t_D$ and $t_{LO}$.

The reset time ($t_R$) is relevant to the memory device and is the time required for bringing the device back to the high resistance OFF state after the setting process is achieved.

The reset pulse gives sufficient energy into the crystallized area of the memory device, which allows the breaking of bonds and diffusion of atoms forming the crystallized material. The subsequent rapid cooling of the material restores the amorphous state.

1.7.4.7 Forming Process

In a threshold switch, any forming process that leads to a material change in the high current density channel must be avoided. The forming process and the material changes due to this, complicate the physical interpretation of the device properties. A forming process may occur when (i) one of the electrodes is oxidized, (ii) the electrode material alloys with the switching material, and (iii) the material in the current filament becomes overheated and tends to phase separate.
These problems can be avoided by a proper choice of device materials and electrodes and by limiting the current in the ON state [Fritzsche, H., 1974].

1.7.5 Factors Affecting the Threshold Voltage ($V_t$) of Chalcogenide glasses

1.7.5.1 Thickness

In amorphous chalcogenide switches, the threshold field ($E_t$) depends on the thickness of the material as shown in the figure 1.15. Thickness dependence of the switching fields can be an indicative of the mechanism of switching involved Kolomiets et al., [Kolomiets et al., 1969] proposed that in thin film of thickness up to 10 μm, the mechanism is electronic. For larger film thickness the threshold field is found to decrease with increase in thickness when thermal effects take over in the switching mechanism as shown in figure 1.15.

The thickness dependence of switching fields can be classified based on the type of the device switch viz., Memory and threshold.

In memory switching chalcogenide glasses the process involved is of thermal origin. The steady state thermal breakdown in homogeneous dielectric slab of thickness 'd' of large area is considered assuming that the electrodes are thin enough so that it does not constitute thermal impediment to the ambient medium [O'Dwyer, J.J., 1973]. Defining the quantities $κ$, the thermal conductivity of the material and $λ$ the external thermal conductivity which quantifies the heat lost by the dielectric through the electrode surface: If $λd ≪ 2κ$, the dielectric behaves as a thermally thick slab and it is thermally
thin if $\lambda d \gg 2\kappa$. In the former case the temperature drop within the material is greater
than the temperature drop at the boundary and a non-uniform temperature distribution
results within the sample. In the later case, the temperature drop at the boundary is
higher due to larger heat loss at the electrodes. Here a uniform temperature distribution
occurs within the sample. $V_t$ has a $d^{1/2}$ dependence for thermally thin slab and a ‘$d$’
dependence for a thermally thick slab [O’Dwyer, J.J., 1973]. Thus, in memory switch
with thermal origin, either a linear or square root dependence for sample thickness with
switching voltage is observed depending on the parameters $\lambda$ and $\kappa$ which are determined
by the electrode geometry, electrode material and the sample.

In bulk chalcogenide threshold switches no much data are available in the
literature for the thickness dependence of switching voltage. However, studies by
Bosnell and Thomas and Kolomiets et al., [Bosnell et al., 1972; Kolomiets et al., 1965]
on Si-Te-As-Ge thin film sample found a linear dependence of $V_t$ with $d$ over a thickness
of 0.1-5 $\mu$m. It was found that higher sample thickness led to a sub-linear dependence,
which can be due to an additional thermal contribution [Kolomiets et al., 1969].

1.7.5.2 Frequency

The frequency dependence of $V_t$ was studied by Haberland et al.,
[Haberland et al., 1970]. The frequency dependence of $V_t$ of a
threshold switch with carbon
electrodes is shown in figure 1.16
[After Sieja, N.F., 1966]. At low
frequencies the rate of change of the
applied voltage is very slow so that
quasi-equilibrium is maintained and
switching is not affected. At high
frequencies $V_t$ drops because of the

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**Figure 1.16:** Typical frequency
dependence of a threshold switching device
[Morin, F.J., 1959].
finite recovery time $t_R$ [Ovshinsky et al., 1973].

1.7.5.3 Temperature

In both threshold and memory devices, $V_t$ is found to decrease with increasing temperature [Ovshinsky et al., 1973]. The magnitude of decrease in $V_t$ with increasing temperature is as shown in figure 1.17 for $\text{Te}_{40}\text{Ge}_7\text{As}_{35}\text{Si}_{18}$, which is a threshold material, and for $\text{Te}_{81}\text{Ge}_{15}\text{Sb}_{2}\text{S}_{2}$, which is a memory material. The temperature dependence of $V_t$ is an important factor which characterizes the thermal degradation and hence the stability of the material for device applications [Algeria et al., 1983].

Figure 1.17: Temperature dependence of threshold voltage of (a) $\text{Te}_{40}\text{Ge}_7\text{As}_{35}\text{Si}_{18}$ (b) $\text{Te}_{81}\text{Ge}_{15}\text{Sb}_{2}\text{S}_{2}$ [Turnbull, D., 1969].

1.8 Optical Properties

In the crystal, the electronic transitions between the valence and conduction bands start at the absorption edge that corresponds to the minimum energy difference $E_g$ between the lowest minimum of the conduction band and the highest maximum of the valence band. If these extrema lie at the same point of the k-space, the transitions are called direct. If this is not the case, the transitions are possibly only due to the phonon-assisted and are called indirect [Tauc, J., 1974]. The governing rule for these transitions is the conservation of quasimomentum during the transition process which may be either due to electron alone leading to direct transitions, or the sum of the electron and phonon quasimomenta in indirect transitions.
In amorphous semiconductors, a shift of the absorption edge is noticed either towards lower or higher energies. In many amorphous compound semiconductors the absorption edge has the shape as shown in the figure 1.18. The absorption can be divided into three distinct regions.

1. The high absorption region A for which $\alpha \geq 10^4 \text{ cm}^{-1}$.
2. The exponential part B, which extends over 4 orders of magnitude of $\alpha$ and
3. The weak absorption tail C.

1.8.1 High Absorption Region

It is often observed in semiconducting glasses that, at high absorption levels ($\alpha \geq 10^4 \text{ cm}^{-1}$) the absorption constant $\alpha$ has the following frequency dependence:

$$\hbar \omega \alpha = (\hbar \omega - E_{g}^{\text{opt}})^r$$  \hspace{1cm} (1.32)

Equation (1.32) has been used to define the optical gap $E_{g}^{\text{opt}}$ as distinguished from the electrical gap $E_{g}^{\text{el}}$ determined from the temperature dependence of electrical conductivity. The range in which the dependence of equation (1.32) is observed is too small to say the exact value of the exponent $r$. The Mott-Cohen-Fritzsche-Ovshinsky model showing the
density of states $g(E)$ as a function of energy in amorphous semiconductors is shown in figure 1.19.

Part A of the absorption curve (figure 1.18) is probably associated with the transitions from the localized valence band states below $E_v$ into the delocalized conduction band states above $E_c^m$ or vice versa. In the empirical relation

$$\alpha h\omega = A(h\omega - E_g^{opt})^2$$

the constant $A$ has been found to be between $10^5$ to $10^6$ cm$^{-1}$ eV$^{-1}$ [Davis et al., 1970]. Davis and Mott interpreted the experimentally observed relation as the transitions from the localized states at the top of the valence band into the delocalized states in the conduction band (or vice-versa).

![Figure 1.19: Density of states $g(E)$ as a function of energy $E$ in amorphous semiconductors, according to the Mott-CFO model. $E_g^{opt}$ is determined by extrapolation of the delocalized states. $E_v^m$ and $E_c^m$ are the mobility edges [Tauc, J., 1974].](image-url)
1.8.2 The Exponential Region of The Absorption Edge

The exponential region of the absorption edge (Part B in figure 1.18) has the following properties

a) In the absorption constant range from 1 cm$^{-1}$ (or less) to about $10^4$ cm$^{-1}$, the absorption constant $\alpha(\omega)$ is described by the formula

$$\alpha(\omega) \sim \exp \left( \frac{\hbar \omega}{E_s} \right)$$

(1.33)

b) The energy $E_s$ characterizing the slope is almost temperature independent at low temperatures (usually below room temperature) and in most semiconducting glasses has the value between 0.05 eV and 0.08 eV.

c) At high temperatures, the slope decreases with temperature [Cervinka et al., 1970].

d) In many amorphous semiconductors parts A and B move as a whole.

1.8.3 Weak Absorption Tail

Below the exponential part of the absorption edge an absorption tail is observed (Part C of figure 1.18). Its strength and shape were found to depend on the preparation, purity and thermal history of the material [Edmond, J.T., 1966; Vasko et al., 1970] even if the material is in the bulk form rather than a film. It is difficult to study this absorption in thin films because of the low absorption levels.
1.9 Rigidity Percolation

The properties of network glasses can be understood using the constraints theory introduced by Phillips, J.C. [Phillips, J.C., 1979; Phillips, J.C., 1981a; Phillips, J.C., 1981b]. This model proposes various properties as a function of the average coordination number $\langle c \rangle$. An assumption is made that the most important forces between the atoms are nearest-neighbor bond-stretching (or central) forces and bond-bending (or angular) forces. Dihedral, van der Waals and other forces are neglected. Thus small displacements from the equilibrium structure can be described by a Kirkwood [Kirkwood, J.G., 1939] or Keating [Keating, P.N., 1966] potential which is schematically written as

$$V = \frac{\alpha}{2}(\Delta l)^2 + \frac{\beta}{2}(\Delta \theta)^2 \quad (1.34)$$

where $\Delta l$ and $\Delta \theta$ are the changes in the bond length and bond angle respectively.

At a critical coordination, the network is flexible and does not resist external strain, since external strain can be accommodated without changing covalent bond lengths and bond angles in the network, so the elastic modulii are zero and remain quite small when the neglected forces are included [Cai et al., 1989]. This implies that during glass formation a cluster which is aperiodic, once nucleated, grows to large dimension without crystallization. At this critical average coordination number, the Glass Forming Tendency (GFT) is maximized.

The concept of percolation in the constraints theory was introduced by Thorpe [Thorpe, M.F., 1983; Phillips et al., 1985]. According to this theory, the network glass consists of floppy or soft regions and rigid regions. At low average coordination the rigid glassy regions forms islands in a floppy background. As the number of bonds or average coordination increases, the rigid islands grow in size and start percolating. This percolating cluster will be infinite in the thermodynamic limit and eventually a percolating rigid cluster emerges. This means that the bond lengths and bond angles
must now be changed at a considerable amount in energy when the network is deformed. It is at this concentration of bonds that the elastic modulii start to become significant. At this stage the percolative rigid cluster gives rise to a transition from an underconstrained or floppy network to an overconstrained or rigid network. The coordination number at which this occurs is referred to as the Rigidity Percolation Threshold (RPT) or Mechanical Threshold (MT). Glasses with average coordination number greater than this critical coordination eventually leads to crystallization.

1.9.1 Chemical Threshold

A second threshold in addition to the mechanical threshold exists in network glasses. According to the Chemically Ordered Covalent Network (COCN) model [Mott and Davis., 1979] the relative strengths of different bonds is crucial in determining the distribution of bonds in the amorphous network. Accordingly, the formation of heteropolar bonds are more likely compared to the homopolar bonds. At a particular composition and coordination number a structure is formed which is maximally ordered comprising of heteropolar bonds. The coordination number at which this occurs is known as the Chemical Threshold (CT). The physical significance of a chemically ordered network is that the glass is energetically closer to the crystalline phase and at CT the materials are bad glass former.

1.9.2 Extended Rigidity Percolation Thresholds

Earlier studies by Phillips [Phillips., 1999] suggest the existence of two rigidity percolation thresholds. In the recent study by Boolchand et al., [Boolchand, P., 2001; Selvanathan et al., 2000; Georgiev et al., 2000] it has been proposed that the rigidity percolation transition occurs over a range of mean coordination numbers leading to three distinct phases namely, floppy, intermediate and rigid.


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