1.1. Introduction

Solid state materials are generally classified into two categories viz. crystalline and amorphous. Crystalline materials are attributed with long-range order in the arrangement of constituents (atoms or ions). Thus, crystalline materials, apart from satisfying valency of the atoms at local sites also have the constraint of atomic arrangement at lattice positions obeying one of the permitted crystallographic symmetries. Many of the physical properties of the crystalline materials can be inferred by knowing the crystallographic space group of the material (Aschroft and Mermin (2001)).

On the other hand, amorphous materials lack the ordered arrangement of atoms (long-range order). However, the valency of the atoms is satisfied, there is variance in nearest neighbor distance, bond length and bond angles, which are generally described by radial distribution function of nearest neighbor atoms in amorphous materials. Figure 1.1 represents the schematic view of the crystalline and amorphous materials. Though the amorphous materials lack long-range order, they certainly have short-range order that might be due to fulfilling the coordination of atoms at local site and represents three dimensional network that lack periodicity and symmetry and known as continuous random network as shown in figure 1.1 (Zachariasen (1932)). The requirement of fulfilling the coordination of atoms at local site is described as 8-N rule by Mott (1969). The presence of short-range order is reflected in many of the physical properties like optical and electronic properties of the materials (Ioffe et al. (1960)). Amorphous materials are generally formed in the process where atoms are restricted for their ordered arrangement to attain the minimum energy configuration (crystalline form being stable with minimum energy configuration). Thus, amorphous materials are actually in the metastable state (i.e. local minimum) and have the tendency to crystallize (i.e. attain global minimum). For some materials, condition of restricting atoms for attaining orderly arrangement is favored while for others it is very difficult to restrict the orderly arrangement of atoms. Consequently, former category represents good glass former and latter represents bad glass former. The examples of good glass former are oxide of group IV elements, which can be made amorphous with ease while it needs very fast quenching techniques to obtain metallic glasses and thus are bad glass former.
Figure 1.1: Crystalline (left part) and amorphous (right part) nature of the material reveals the orderly/disorderly arrangement of atoms in material.
In case of oxides of group IV elements, bonds are covalent and directional, that make the molecular structure rigid and thus viscous. This leads to restricting the free movement of atoms and thus avoiding crystallization in the material. While in case of metallic glasses, there is a free movement of atoms in the molten state, which can only be avoided by practicing very fast quenching of material from molten state and thus not providing enough time for atoms to move and orderly arrange to achieve crystallization in the material. Figure 1.2 represents the volume-temperature diagram depicting liquid-solid transition. In case of crystalline materials, there is sharp and discontinuous drop in volume at characteristics temperature $T_m$ called melting temperature followed by marginal change in volume on further cooling. For amorphous solids, the decrease in volume is continuous and gradual with decrease in temperature. The change in the slope of volume-temperature curve is characterized with glass transition and corresponding temperature is glass transition temperature.

1.2. Amorphous Semiconductors and its Classification

The amorphous materials can be divided into three categories viz. conductor, semiconductor and insulator depending upon their conductivity and band gap. Metallic glasses represent the category of amorphous conductor because of high conductivity and absence of any quantum mechanically inaccessible energy range above Fermi energy level. The second category of amorphous materials is wide variety of oxide glasses that generally represents the category of amorphous insulator. These materials have very low conductivity and large band gap $\geq 3$ eV. The third category of amorphous materials is widely represented by two group of materials namely tetrahedrally bonded amorphous semiconductor and chalcogenide semiconductor, while some of the oxide glasses come under amorphous semiconductor regime also due to their high conductivity range. These materials have conductivity in the range $10^{-13} - 10^2$ Scm$^{-1}$ and have optical band gap in the range 1-3eV. The lack of long range periodicity and variance in the bond length and bond angle (topological disorder) in the amorphous materials causes two major effects. The first effect is tailing of the band edges into band gap because of the local potential fluctuations introduced by variation in bond length and bond angles. The second effect is localization of some of the electronic states in the sense that electronic wave function has finite value in limited space and zero everywhere else (Anderson (1958)). It was later on shown that not all the extended states of the crystalline material can be made localized by disorder and the process of localization occur for only tail states beyond the band edges.
Figure 1.2: Volume-temperature plot during cooling of liquid. The sharp and discontinuous drop in volume is characteristics for crystalline material and continuous and gradual decrease of volume is characteristic of glasses.
The situation of band structure for amorphous semiconductors is represented in figure 1.3. The left part of the figure depicts the case of perfectly crystalline semiconductor, middle part shows the smearing out of the electronic states near band edges caused by topological disorder shown as shaded area with set of parallel lines and the right part represents the case of amorphous semiconductors with both topological disorder and bonding defects causing density of localized states near Fermi level. Table 1.1 represents the examples of three different types of amorphous semiconductors.

1.3. **Amorphous Chalcogenide and Band Models**

Amorphous chalcogenide semiconductors represent a class of materials that have interesting and quite different physical properties from basic physics point of view. These materials consist of dominant or entirely group VI chalcogen elements (S, Se, and Te) that have two-fold coordination for chalcogen atoms and thus provide greater flexibility for atomic movement in these materials. The chalcogen atoms exist in linear chain structures which are three dimensionally connected through non-chalcogen, group IV and V atoms. The chalcogen atom has six electrons in its valence shell, two of which occupy the deep lying s-orbital with opposite spin. The remaining four electrons occupy the three degenerate p-orbitals with two electrons out of four, paired and remaining two electrons unpaired. The two unpaired electrons participate in bonding of chalcogen atom with another chalcogen or non-chalcogen atom. Bonding (interaction with another atom) of chalcogen atom lifts the degeneracy of the p-orbitals and p-orbitals split up on energy scale with reference to the p-orbital paired electrons called ‘lone pair’. Since the interaction of chalcogen atom with another atom does not affect the energy of lone pair electrons because of the fact that it cannot participate in bonding due to full occupancy of the orbital. The other two unpaired orbital’s participating in bonding split up into bonding (\(\sigma\)) and anti-bonding (\(\sigma^*\)) levels lying below and above the lone pair level on energy scale respectively. Following Hund’s rule and Fermi statistics, the electrons occupy the low lying bonding (\(\sigma\)) level leaving anti-bonding (\(\sigma^*\)) level unoccupied as shown in figure 1.4. Now considering the case of a solid containing ~ \(10^{23}\) atoms, the molecular bonding, lone pair and anti-bonding levels broaden into their respective band containing large number of quasi-continuous energy levels with very small inter-level energy as shown by shaded area in the right side of figure 1.4. the band due to lone pair levels lie above the band due to bonding states and thus serve as valence band (band having energy levels occupied with electrons) and band due to anti-bonding levels serve as conduction band.
Figure 1.3: The band structure of (a) crystalline, (b) amorphous (topological disorder) and (c) amorphous (topological disorder and bonding defects).
Table 1.1: The different classes of amorphous semiconductors.

<table>
<thead>
<tr>
<th>Amorphous semiconductors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedrally bonded semiconductors</td>
</tr>
<tr>
<td>Si, Ge</td>
</tr>
<tr>
<td>InSb, GaAs, GaSb, SiC</td>
</tr>
<tr>
<td></td>
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<td></td>
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</tbody>
</table>
Figure 1.4: The energy levels for isolated chalcogen atom, for two bonded chalcogen atoms and energy band for chalcogenide solid material.
(band having its energy levels unoccupied at absolute zero temperature) and there exists a gap \( \sim 1-3 \) eV on energy scale between valence and conduction band characteristics of semiconductors. The critical difference of chalcogenide semiconductors from other tetrahedrally bonded semiconductors is that the valence band in case of chalcogenide semiconductors originate from lone pair states of the chalcogen atoms and not from the bonding states that affect many physical properties of these materials and thus these materials are called lone pair semiconductors.

The chalcogenide materials when prepared in amorphous form have profound effects on the band structure of these materials with the introduction of several types of disorders in the material. There is topological disorder due to variance in the bond length and angles, lack of long range order in the material, structural disorder due to bond breaking (due to topological disorder) and presence of under-coordinated atoms at the end of chains (dangling bonds) that creates large density of structural defects in the material and at last compositional disorder due to chemical inhomogeneity in the structural units of the materials. Different band models for amorphous semiconductors have been proposed by many researchers to account for the changes on the band structure of the material and thus explanation of observed physical properties of the material. In the following subsections, various band models for amorphous chalcogenide materials are briefly discussed.

### 1.3.1. Cohen, Fritzscne and Ovshinsky Model

This was the first model for amorphous semiconductors given by Cohen, Fritzscne and Ovshinsky in 1969 to account for the observed physical properties of amorphous semiconductors. Main feature of the model was overlapping of conduction and valence band tail states that originate from localization of charge carriers due to topological disorder present in the material. The topological disorder in such materials is assumed to be appreciable enough that most of the atoms satisfy their valences keeping the concept of extended states of valence and conduction band valid (Mott (1970)). Thus the topological disorder affects the band tailing of valence and conduction band in a way to introduce localized states adjoining the sharp band edges. These states are localized in the sense that the wave-function is exponentially decaying around the centre of localization and charge trapped cannot itinerate throughout the material. Despite the overlapping of valence and conduction band tail states, there is sharp decrease in the mobility of charge carriers for
localized states compared to the extended states and thus mark the band edges for amorphous semiconductors known as mobility edges. The generalized band structure of the amorphous semiconductors is shown in figure 1.5 based on the concept of model given by Cohen *et al.* (1969). The overlapping of band tail states implies that in some region of the material, there might be electrons in the valence band having higher energy than the electrons in the nonbonding state comprising conduction band. Thus such electrons make transition to conduction band states having lower energy and corresponding empty states in valence band and occupied states in conduction band tail act as positive and negative charge trapping centers. The appreciable density of localized defect states around Fermi level effectively pins the Fermi level making these semiconductors intrinsic in nature (Pearson (1964) and Kolomiets (1964)). The presence of mobility edges in the amorphous semiconductors justifies the thermally activated conduction process with well defined thermal activation energy in these materials. The electrical transport at low temperature is due to thermally activated hopping conduction between localized states (Mott and Twose (1961) and Mott (1968)).

1.3.2. *Davis and Mott Model*

This model has been proposed by Davis and Mott (1970) to explain the observed electrical properties of amorphous semiconductors such as Photoconductivity (Main (1973)), photoluminescence (*Street et al.* (1973, 1974a)), field effect, drift mobility (Marshall and Owen (1971)) measurements and pinning of Fermi level in amorphous chalcogenide semiconductors that revealed the presence of high density of localized states in the band gap of these materials. This model described the high density of localized states as associated with the neutral dangling bonds $D^0$ present in these materials. The chalcogenide materials having two fold coordination has linear chain structure with appreciable number of under-coordinated chalcogen atoms at the end of chain that act as dangling bonds and thus introduce point defects in the material. These neutral dangling bonds have one unpaired electron and introduce energy level in the middle of the band gap around Fermi level that effectively pins the Fermi level. The schematic diagram of the band structure as proposed by this model is given in figure 1.6. This model also showed the presence of mobility edges marked $E_C$ and $E_V$ across the extended to localized states. The major difference of this model from the earlier one was non-monotonic decay of density of states (DOS) in the band gap region and appreciably high DOS in the middle of band gap around Fermi level due to dangling bonds.
Figure 1.5: (a) band model for amorphous semiconductors and (b) mobility edges for charge carriers in amorphous semiconductors as given by Cohen, Fritzsche and Ovshinsky (Cohen et al. (1969)).
Figure 1.6: The band model for amorphous semiconductors given by Davis and Mott (Davis and Mott (1970)).
1.3.3. **Mott, Davis and Street Model**

This model was put forward by Mott, Davis and Street (Mott et al. (1975) and Street and Mott (1975)). Despite explaining many of the physical properties of the amorphous semiconductors, the major drawback of the earlier model was prediction of electron spin resonance (ESR) signal arising from unpaired electron of neutral dangling bond. While experiments demonstrated the absence of any such signal observed for chalcogenide semiconductors (Aggarwal (1973)) along with curie paramagnetism at low temperature (DiSalvo et al. (1972)) indicating the absence of free spins at equilibrium. Following the idea of negative effective correlation energy, $U_{\text{eff}}$ for pairing of spins at single defect site in amorphous chalcogenide semiconductors given by Anderson (1975), experimental findings of charged radiative recombination center from photoluminescence studies (Street et al. (1973)), presence of stokes shift (Street et al. (1974a, and 1974b)), they put forward a model of amorphous chalcogenide semiconductors having charged $D^+$ and $D^-$ defect states instead of neutral $D^0$ dangling bonds that serve as deep acceptor and donor levels in these semiconductors. The schematic representation of band structure for this model is shown in figure 1.7. The peaks of defect DOS in the band gap region marked $E_X$ and $E_Y$ represent the localized levels for $D^+$ and $D^-$ dangling bonds respectively. Large flexibility in these materials lead to the possibility of strong lattice distortions in order to achieve charged defect states instead of neutral dangling bonds that are only being created during external excitation as has been observed in photo-induced ESR signal (Bishop et al. (1975, 1977 and 1979)) and photocurrent decay in chalcogenide materials. Thus this model is most satisfactory in explaining the physical properties of amorphous chalcogenide semiconductors.

1.4. **Defect States in Amorphous Chalcogenide Semiconductors**

As already discussed in the section above that amorphous chalcogenide semiconductors have quite different and unusual properties from tetrahedrally bonded amorphous semiconductors regarding absence of ESR signal (Aggarwal (1973)), curie paramagnetism at low temperature (DiSalvo et al. (1972)) and variable range hopping (Mott and Davis (1979)) and effective pinning of Fermi level (Mott and Davis (1979)) in the mid-gap of the semiconductor revealed the absence of unpaired spins in these materials. Moreover other experimental findings like photoluminescence (Street (1976)), photoconductivity (Arnoldussen et al. (1972, 1974) and Bube (1992)), drift mobility
Figure 1.7: The band model of amorphous semiconductors given by Mott, Davis and Street (Mott et al. (1975) and Street and Mott (1975)).
(Marshall and Owen (1971)) and field effect studies (Marshall and Owen (1971)) revealed the presence of high density of states in the band gap region that pins the Fermi level in these materials. Davis and Mott (1970) related these defects with the neutral dangling bonds having single unpaired electron and are present at the ends of chain structure in these materials. But that idea did not explain the experimental finding of absence of unpaired spin in these materials. The first model of paired spins was introduced by Anderson (1975) explaining the possibility of formation of paired spin at same site and thus, explaining the absence of ESR signal in chalcogenide materials. He found the effective correlation energy for pairing of two spins at same site can be made negative through strong electron-phonon coupling that lowers the energy of the system below that of singly occupied unpaired spins as in the case of neutral dangling bonds. The chalcogenide materials having highly flexible structure due to two fold coordination provide the required strong electron-phonon coupling by introducing lattice distortions in the system and thus allow the lowering of system’s energy by spin pairing. The potential energy for the system is thus written as

$$V = \frac{C\lambda^2}{2} - \lambda x_i (n_{i\uparrow} + n_{i\downarrow})$$

That gives the effective correlation energy $U_{eff}$

$$U_{eff} = U - \frac{\lambda^2}{C}$$

The effective correlation energy can be made negative if the electron-phonon coupling $\lambda$ can be made sufficiently large. Later on Mott, Davis and Street (Mott et al. (1975) and Street and Mott (1975)) asserted that the pairing of spins lead to formation of negative charged defect, $D^-$ states in these materials and charge neutrality asserts formation of equal density of positive charge defect, $D^+$ states (Mott et al. (1975)). The conversion of neutral dangling bonds into charged defect states is represented with the reaction that should be exothermic as given.

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

The $D^-$ defect state represents the paired electron at the end of chain structure and $D^+$ defect state represents the three coordinated chalcogen atom in the material as shown in figure 1.8(a). The conversion of the neutral dangling bond into charged defect states along
with negative effective correlation energy for the reaction in energy-configuration coordinate diagram is shown in figure 1.8(b). The coulombic repulsion for putting two electrons at the same site, $U$ that can be more than compensated by relaxation through lattice distortion that leads to lowering of system energy.

Kastner, Adler and Fritzsche (Kastner et al. (1976)) described the different possible bonding configurations for chalcogenide materials. They used the notation of $C_p^x$ for describing the configuration of atoms. Superscript $x$ denotes the charged state and subscript $p$ denotes the coordination of the atom at particular site. The different possible configurations for atoms in chalcogenide materials are shown in figure 1.9 along with energy of formation of these configurations. The lines in configuration sketch represent bonding state, lobes represents non-bonding state and circle represents anti-bonding state. The electrons are represented with arrows in non-bonding and anti-bonding states with arrow head showing spin direction. The formation energy of the configuration is with reference to lone pair level. For calculating the energy of formation for particular configuration, they used the approximation that placing single electron in bonding state $(\sigma)$ costs $-E_b$ and in the anti-bonding state $(\sigma^*)$ costs $E_b + \Delta$ because of asymmetry in level splitting (Kauzmann (1957)). Moreover an additional electron placed on an atom costs correlation energy $U^*$ or $U_{LP}$ depending upon whether electron is placed in linear combination of anti-bonding states or lone pair state respectively. They assumed that correlation energy $U^*$ or $U_{LP}$ for additional electron is smaller than $E_b$ (level splitting).

Normal two-coordinated atom $C_2^0$ has lowest energy $-2E_b$ and thus most stable, the other neutral three fold $C_3^0$ configuration and neutral one fold configuration $C_1^0$ has bond formation energies $-2E_b + \Delta$ and $-E_b$ respectively. Since the configuration $C_1^0$ is unfavorable because it require full $E_b$ energy for formation and configuration $C_3^0$ is lowest energy defect and favorable but is not stable and converts into $C_3^+ \text{ and } C_3^-$ through charge transfer reaction since that demand only $U^*$ energy.

$$2c_3^0 \rightarrow c_3^+ + c_3^-$$

The positive three coordinated defect $C_3^+$ converts into positive singly coordinated defect $C_1^+$ through nearest neighbor $C_2^0$ as given by reaction.

$$c_3^- + c_2^0 \rightarrow c_2^0 + c_1^-$$

For the reaction to be exothermic, $2\Delta - (U_{LP} - U^*)$ should be positive and thus system can
Figure 1.8: (a) The pictorial representation of positive and negative charged defects formation from neutral dangling bond pair through exchange of electron and (b) energy-configurational graph representing negative effective correlation energy for the reaction.
Figure 1.9: The various possible configurations of chalcogen atom in amorphous state along with their formation energy with respect to Lone pair level (Kastner et al. (1976)).

<table>
<thead>
<tr>
<th>Configuration</th>
<th>p-level occupation</th>
<th>Energy/configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2^0$</td>
<td>![Diagram of $C_2^0$]</td>
<td>$-2E_b$</td>
</tr>
<tr>
<td>$C_3^0$</td>
<td>![Diagram of $C_3^0$]</td>
<td>$-2E_b + \Delta$</td>
</tr>
<tr>
<td>$C_3^+$</td>
<td>![Diagram of $C_3^+$]</td>
<td>$-3E_b$</td>
</tr>
<tr>
<td>$C_3^-$</td>
<td>![Diagram of $C_3^-$]</td>
<td>$-E_b + 2\Delta + U_{\sigma^*}$</td>
</tr>
<tr>
<td>$C_1^0$</td>
<td>![Diagram of $C_1^0$]</td>
<td>$-E_b$</td>
</tr>
<tr>
<td>$C_1^-$</td>
<td>![Diagram of $C_1^-$]</td>
<td>$-E_b + U_{LP}$</td>
</tr>
</tbody>
</table>
lower energy by transferring the two bonding and two anti-bonding electrons of \( C_3^- \) configuration into lone pair states of \( c_1^- \) configuration. The net reaction is

\[ 2c_3^0 \rightarrow c_3^+ + c_1^- \]

The charged configurations \( c_3^+, c_1^- \) are similar to the charged defect states described by Mott, Davis and Street (1975). Since the creation of charged configurations \( c_3^+, c_1^- \) are linked and thus called Valence alternation pair (VAP). If the distribution of VAP’s is nonrandom and pair is attached with coulombic attraction, then it is called intimate VAP and other wise non-intimate VAP. These VAP’s introduce energy levels in the band gap region. Under equilibrium conditions, there is equal concentration of both \( c_3^+ \) and \( c_1^- \) and gives rise to levels A and A’ under optical excitations as depicted in figure 1.10. There will be energy difference for thermal transitions involving lattice deformation from optical transitions not involving lattice deformation. If a \( c_3^+ \) captures an electron either from conduction band or by photo-excitation from valence band, a \( c_3^0 \) center is formed with spectrum of levels as shown in the middle part of the figure 1.10. This \( c_3^0 \) center is amphoteric in nature and can act as donor (levels B and C) or acceptor (levels B’ and C’). In the configuration-coordinate, levels B and B’ represent the non-vertical, thermal transitions while the levels C and C’ represent vertical optical transitions. Removal of an electron from the \( c_3^0 \) restores \( c_3^+ \) center either by thermal or optical transition. Similarly the addition of an electron to \( c_3^0 \) creates \( c_3^- \) center with correlation energy \( U^* \) for placing electron in anti-bonding state that pushes the C’ level above C level. This \( c_3^0 \) center is unstable and thus converts into \( c_1^- \) center. The various optical and thermal transitions are summarized in reaction-form below (Benkhedir (2006)).

**Optical transitions**

\[ C_3^+ + e_{VB} + (E_1 + W^+) \rightarrow C_3^0 \]

\[ C_3^0 + (E_g - E_1 + W^+) \rightarrow C_3^+ + e_{CB} \]

\[ C_3^0 + e_{VB} + (E_2 + W^+) \rightarrow C_3^- \]

\[ C_3^- + (E_g - E_2 + W^+) \rightarrow C_3^0 + e_{CB} \]

and thermal transitions

\[ C_3^+ + e_{VB} + (E_1) \rightarrow C_3^0 \]
Figure 1.10: The band structure representing charged and neutral defect energy levels in amorphous semiconductors after Kastner et al. (1976).
These levels have been experimentally found in chalcogenide materials (Street (1976)) and explains the presence of stokes shift in photoluminescence of chalcogenide materials. The above discussed configurations were in the context of chalcogen atoms in chalcogenide materials and there are other possible configurations for non-chalcogen atoms in chalcogenide materials due to their under or over-coordination in the material that also introduces charged and neutral defect levels in the band gap region. The possibility of such defect configurations was treated by (Adler (1980), Vanderbilt and Joannopoulos (1981) and Kastner et al. (1976)). They used the letter P and T for group V and Group IV elements respectively to discuss different possible configurations of non-chalcogen atoms in chalcogenide materials.

Adler and Yoffa (1976) calculated the Fermi energy as a function of temperature and electronic density and concluded the pinning of fermi level within the charged defect states for negative correlation energy system. They also reported that fermi level lies below the highest filled quasiparticle level and thus explains the origin of p-type nature of these semiconductors. The results of their calculations were summarized in figure 1.11 depicting density of defect levels for both (a) positive and (b) negative correlation energy system (upper part) along with movement of fermi level with defect state occupancy ‘n’ (lower part). Figure 1.11 represent a semiconductor with conduction and valence band edges $E_C$ and $E_V$ and an empty defect state localized at ‘$T_0$’ level in the band gap region. For positive correlation energy system, the level would be filled upto fully single occupancy and as double occupancy starts to prevail, the defect level rises to $T_0 + U$ value, thus shifting the fermi energy discontinuously from $T_0$ to $T_0 + U$ as shown in figure 1.11. In case of negative correlation energy system, electrons are placed in level $T_0$ until full single occupancy is achieved and $n=1$. On further placing the electrons fills the level with energy $T_0 - |U|$ that is less than $T_0$. Thus fermi level lies below the highest occupied level leading to effectively pinning the fermi level as shown in figure 1.11.

1.5. Applications of Chalcogenide Semiconductors

Chalcogenide materials find many applications in electronic, optical, optoelectronic devices and other technological fields due to their unique properties. Some
Figure 1.11: The defect density for single defect $T_0$ (upper part) and Fermi energy as a function of occupancy (lower part) for (a) positive correlation energy system (b) for negative correlation energy system (Adler and Yoffa (1976)).
of the current and upcoming applications of chalcogenide materials are discussed in following sections.

1.5.1. Phase change based optical and electronic memories

The unique property of chalcogenide materials to be stable in both amorphous as well as crystalline phase at moderate temperature and fast transition rate from one phase to another with appreciable physical property contrast for the two phases makes these materials useful for data storage memory applications. The chalcogenide materials that exhibit the above said properties are known as ‘phase change materials’ (PCM). High optical reflectivity contrast and electrical resistivity contrast for the two phases of these materials are utilized for memory storage and thus used for optical data storage media (DVD, CD) and phase change random access memories (PCRAM). The widespread application of these PCM’s is due to their simplicity in the working and thus better device performance based on these materials compared to earlier available storage devices (magneto-optical disk). Since the observation of reversible switching (Ovshinsky (1968)) in chalcogenide materials, its potential application for optical and electrical memories was explored (Ovshinsky and Fritzsche (1973)) and later on phase change materials for optical media were investigated in late 1980’s (Yamada et al. (1987 and 1991), Chen et al. (1986)) with high switching rates. The use of phase change materials for PCRAM (electronic memory) is recently being explored (Pirovano et al. (2004), Wuttig (2005), Lankhorst et al. (2005) and Bruns et al. (2009)) as an alternative to existing memories as further scaling down of the existing RAM technologies become limited. The working principle of phase change material for optical media as well as electronic memory is described in figure 1.12. The PCM in the active device area is made amorphous by intense laser beam or electric pulse (RESET pulse) to raise the temperature of the material above melting temperature $T_m$ which then rapidly quenched into low reflectivity and high resistivity amorphous phase that serve as binary ‘0’ for data storage. The amorphous phase can be converted to highly reflective and low resistive crystalline phase by moderate laser beam or electric pulse (SET pulse) by raising its temperature above glass transition $T_g$ that serve as binary ‘1’ for data storage. This is how data is being written, erased and re-written onto phase change material and data is read with the help of low power laser beam or electric pulse to know the state of the PCM in the active region without disturbing it. Though the reflectivity change between the two phases is around 30% while there is around two-three order of magnitude change in resistivity is observed for PCM’s.
Figure 1.12: The schematic of process of phase change by application of Laser power/electric pulse along with peculiar properties of the obtained phases.
The switching of crystalline to amorphous phase is achieved by laser heating of active region for optical media while the same is achieved through joule heating for electronic memories. I-V characteristics of a typical PCM memory cell is described in figure 1.13. When voltage is applied to cell that is prior in amorphous high resistive state, very low current flows through it until threshold voltage is approached where material undergoes a fast electronic transition (threshold switching (Adler et al. (1978)) and conductivity of material increases while in amorphous state. This increased conductivity triggers the joule heating in the material for transforming into crystalline state that leads to memory switching. The mechanism of threshold switching and value of threshold voltage play critical role for a material to be good PCM and thus should be properly understood.

Two different cell designs are currently used for PCRAM cells. The first one is called Ovonic unified memory (OUM) by many researchers and the second is line design adopted by (Lankhorst et al. (2005)). The design description of both architectures is shown in figure 1.14. The first design envisage the use of phase change material in simple structures deposited between two electrodes along vertical axis where the bottom electrode serve both as electrical contact as well as heat source for PCM leading to switching of the active area in mushroom head shape as shown in the upper part of the figure 1.14 (Lelmini et al. (2004)). The line design uses lithographic patterning and other semiconductor processing techniques for cell manufacturing and has one advantage of better adherence of electrodes at high temperature that cause problem for efficient working of the cell. Many chalcogenide compositions have been studied for Phase change memory applications and performance is limited to phase transition kinetics and rate of switching. Commonly studied compositions for PCM are given in table 1.2.

1.5.2. Optical fibers

The chalcogenide glasses exhibit very good transparency in the infrared range from ~ 1-12μm depending upon the composition of the materials. The chalcogenide materials containing S, Se and Te transmit in the 0.8-7, 1-10, and 2-12μm, range respectively (Sanghera and Aggarwal (1999)). For device applications in the IR region of the spectrum, the transparency in the range 3-5μm and 8-14μm is required, where the atmospheric absorption is a minimum. The chalcogenide glasses are attributed with high optical bandgap, long wavelength multiphonon edge and low optical attenuation and are chemically stable in air and can be easily drawn into long core-clad fibers.
Figure 1.13: The typical I-V behavior of Phase change material used for PCRAM (Wuttig and Yamada (2007)).
Figure 1.14: Two different configurations used for PCRAM’s. Top configuration is OUM (Ovshinsky (1968)) and bottom one is Line configuration (Lankhorst et al. (2005)).
Table 1.2: The commonly studied compositions for phase change materials in optical data storage and PCRAM.

<table>
<thead>
<tr>
<th>Binary</th>
<th>Ternary</th>
<th>Quaternary</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbTe, InSe, SbSe, GeTe</td>
<td>GeSbTe, InSbTe, InSeTl, GeTeTi, GaTeSe, GeTeAs, SnTeSe, GeTeSn, SbSeBi</td>
<td>GeSbTeN, GeSbTeNi, GeSbTeSe, AgInSbTe, GeTeSnPd, GeTeSnAu, GeTeSnO, InSeTlCo</td>
</tr>
</tbody>
</table>
The impurity scattering reduces the transparency of chalcogenide glasses in these regimes, and can be controlled by careful processing and improved purification methods (Sanghera and Aggarwal (1997)) that make these materials prospective candidates for active and passive device applications (Miyashita and Manabe (1982)). Passive application involve use of chalcogenide optical fibers as light conduit pipe for transmission from one place to another with no change in signal strength other than scattering, absorption and end face reflection while active application involve modification of signal strength through processes other than scattering, absorption and end face reflection originating from nonlinear effects in optical properties of these materials. Thus these materials are utilized in commercial and technological applications like telecommunication, thermal imaging, remote sensing, and laser power delivery etc. some of which are described below briefly.

**Laser power delivery**

High power CO and CO$_2$ laser at 5.4 and 10.6 μm respectively are used for industrial welding and cutting applications and thus require remote operation by transmitting laser power through the optical fibers. The chalcogenide As-S based fibers are used to deliver high-power laser light due to high transmittance in the wavelength range of laser operation and lower damage and high tolerance for power densities ~ 125KW/cm$^2$ at 5.4 μm wavelength (Busse et al. (1996)) without any nonlinear effects. These fibers can also be used for military applications as in infrared countermeasures and laser threat warning systems. Another area of laser power delivery using these fibers is in transmitting medical free electron laser for surgery, machining of materials and biological samples.

**Remote sensing and thermal imaging**

Different sensing techniques viz. attenuated total reflectance, diffused reflectance are used for chemical detections in mixtures, contamination (Nau et al.(1996)) that involve use of these fibers to transmit signals from remote areas. Since detection of different aqueous, non-aqueous, toxic chemicals, paints, polymers and pharmaceutical products involve sensing and transmitting characteristic vibration frequency of the molecular species and thus require chalcogenide glass fibers (Heo et al. (1991) and Dury (1998)). These fibers are also used for condition based maintenance in quality control and for reduction of operating cost of and for bio-medical tissue detection for disease diagnosis. Chalcogenide glasses based fibers are also used for thermal, hyper-spectral and IR images. This was first demonstrated by Nishii et al. (1991) by taking thermal images of an operating integrated circuit in the 3- 5.4μm range.
1.5.3. IR signal amplification and all optical switching

IR signal amplification and laser action can be invoked in the material having low phonon energy such as chalcogenide glasses that can activate the transitions between energy level of doped rare-earth elements in chalcogenide glasses and is thus useful in many device applications such as bright source, laser for optoelectronic devices (Schweizer et al. (1997)). Most commonly doped rare-earth elements in chalcogenide materials are Pr$^{3+}$, Dy$^{3+}$ and Er$^{3+}$ and Nd$^{3+}$ ions with IR emission 1.34, 1.08 $\mu$m wavelengths. Amplification of IR signal was first observed for Nd$^{3+}$ doped Ge-As-Ga-Sb-S glass at 1.08 $\mu$m wavelength (Mori et al. (1997)). The challenge in this field is for obtaining a material that has higher rare-earth element solubility so that higher gain can be achieved for better device performance. Ga-La-S based glasses showed excellent solubility for rare-earth elements and are prospect materials for IR signal amplification (Ye et al. (1996) and Schweizer et al. (1997)).

Another application for chalcogenide materials is all-optical switching that will pave way for high speed optical communication for data transmission and for high speed optical based computing. The concept is based on guiding flow of light by another light that will drastically increase the speed of communication devices. To accomplish the all-optical switching high nonlinearity, high power density and sufficient long interaction length of device is demanded that can be fulfilled using chalcogenide glasses having higher value of linear refractive index along with high non linear refractive index, low to moderate two photon absorption at wavelengths longer than electronic absorption edge and can be easily fabricated in optical fiber and waveguide structures due to stable glass structure. Owing to all these features of the chalcogenide glasses, these materials find very good prospects for high speed computing and communication devices. Many preliminary experiments have recently been conducted to design and fabricate devices based on non linear refractive index for switching light by another trigger of light, some of which are optical Kerr shutter, nonlinear optical loop mirror (Asobe (1997)), brag mirror (Baumgartner et al. (2006)), high quality gratings, signal regeneration and compression (Taeed et al. (2007)), long period gratings (Nguyen et al.(2008)), omnidirectional photonic band gap IR filter (Kondakci et al.(2009)) and planar wave guide (Ganjoo et al. (2006), Juejun et al.(2010)).
1.5.4. Chemical sensors

Another application of chalcogenide glasses is its use as membrane material in chemical sensors, microsensors and multisensor systems. These materials are used as functional membrane in ion-selective electrodes (ISE) (Vassilev and Boycheva (2005)) because of good chemical durability of these materials in both acidic and redox environment. Simple construction and low maintenance of these material based sensors make them preferred choice for many ions determination like Ag$^+$, Cd$^{+2}$, Pb$^{+2}$, Cu$^{+2}$, Hg$^{+2}$, Fe$^{+3}$ and Zn$^{+2}$. Moreover these sensors are successfully applied for determination of inorganic pollutant in rivers, ground, sea and waste water, for corrosion process monitoring (Legin et al. (1995) and De Marco and Shacleton (1999)). These chalcogenide sensors have stable linear electrode function in the concentration range 10$^{-6}$-10$^{-1}$ mol/ltr achieved after conditioning in the concentrated solution of potential determining ion (Frazer and Owen (1983)) with response time varying from few seconds to about a minute depending upon diffusion coefficient of potential determining ion and nature of the glassy membrane. The ion selectivity and sensitivity of these chalcogenide glassy materials is understood in terms of redox processes taking place at the membrane- solution interface forming modified surface layer (Owen (1980) and Tohge and Tanaka (1986)).

1.5.5. Photolithography

Chalcogenide glasses find another utility of being used as photo-resist in the photolithography pattern formation. This utility of chalcogenide glasses originate from the photosensitive response of these materials and can be used to produce high-resolution replica of complex patterns. Chalcogenide glasses exhibit unique property of Photo-dissolution of metals like silver, copper etc that leads to change in the physical properties of the complex that is utilized for creating patterns and has generated interest in this field. Photolithography with chalcogenide glass is very similar to the conventional organic-resist process (Tanaka (1991)). A film of chalcogenide glass is deposited on the substrate to be patterned using standard deposition techniques including thermal evaporation, sputtering, and chemical vapor deposition. A thin layer of silver is then deposited over the already deposited chalcogenide glass and the sample is then exposed to incident light through the desired pattern. Silver diffuses into the area of chalcogenide glass illuminated through the pattern. The area of chalcogenide glass devoid of dissolved metal is then removed by wet or dry etching leaving behind a negative resist. Such a process is easy to incorporate in the current semiconductor fabrication processing. With proper methods and optimization,
patterns of dimensions ~10 to 50 nm can be generated. Kolobov (1993) has demonstrated the formation of ~60 nm structures using electron-beam exposure with dry etching.

1.5.6. Photoconductor for X-ray imaging and vidicon tube

Amorphous chalcogenide materials especially elemental Se or Se based alloys are widely used as photoconductors for various optoelectronic applications. These materials are used in X-ray photo-detector (Kasap and Rowlands (2000)) and high gain avalanche rushing photoconductor in highly sensitive video tubes (HARPICON) (Kubota et al. (1996)). These are also used in electro-photographic imaging devices and ultra sensitive CMOS image sensor (Toshisha et al. (2003)). In high gain avalanche rushing photoconductors, an electron-hole pair is produced by an incident photon and the generated photo-carriers are then accelerated by the large electric field applied to an $a$-Se target. These accelerated carriers produce more and more electron-hole pairs through impact ionization. The impact ionization phenomenon occurs repeatedly inside the target and thus leads to an avalanche effect (Arkhipov and Kasap (2000)) that enables the video tube to capture clear images with full color reproduction even in the dark. Since the sensitivity of the camera can be varied over a wide range by changing the voltage applied to the target, the device can be used during daytime or under normal lighting conditions.