CHAPTER ONE
CHAPTER - ONE

CHALCOGENIDE GLASSES

1.1 An Introduction:

Physics deals with the study of the fundamental laws of nature, which govern the behavior of all matters. The science and technology of materials are constantly undergoing vital changes. We have now entered into an age of materials science where-in materials go by a variety of interpretive names such as smart, intelligent, high performance, hi-tech, tailored, engineered etc. The suitability of the materials for high technology applications requires additional information about the material in respect of optical, structural and electrical characterization. Characterization of materials from optical, structural and electrical consideration involves the determination of features such as optical band gap, nature of band gap, crystallographic structure, chemical composition and current voltage characteristics of the materials. The information about these features is significant for the reproduction of materials. Semiconductors are the basic components of the integrated circuits and are responsible for the starting rapid growth of the electronics industry in the past fifty-to-sixty years worldwide. Because there is a continuing need for the faster and more complex systems for the information era, existing semiconductors are being studied for improvement,
and new ones are being invented. Whether it is for higher speed, lower power, higher density, higher efficiency, or new functionality, the number and types of semiconductors have been growing steadily in the fascinating field.

It is difficult to have a clear quantitative definition of semiconductor. Based on conductivity, materials can be classified into three groups: (i) metal (ii) semiconductor, and (iii) insulator. It is to be noted that the most important feature of the semiconductor is that it can be doped with impurities to different concentration levels, so ever semiconductor material can cover a range of conductivity.

The earliest device, not necessarily made of semiconductor material, is probably the resistor, implied by Ohm's law back in 1826. Vacuum tubes started around 1904, and were the major electronic components in the early radio era through World War II. The real world of the semiconductors was in 1947 with the invention of the bipolar transistor.

According to their properties and behavior, Materials can be classified as crystalline and non-crystalline solids. In a crystal, the atoms are arranged in a periodic repeated pattern, whereas no such regularity occurs in non-crystalline material. Again crystalline solid can be divided into two as single crystal, where entire solid consists of only one crystal and polycrystalline, where the solid has an aggregate of many crystal separated by well defined boundaries.

Optical properties of amorphous and crystalline semiconductors are of special interest. Recent years have seen an upsurge in interest in the electronic properties of non-crystalline materials. These lack the simple structures and long
range order that make crystals relatively easy to understand. The interest, both at Sheffield and worldwide have largely concentrated on amorphous silicon and its relatives. A wide variety of measurements have made along with the photoluminescence methods, for a broad understanding of the semiconductors. These materials are widely used in Xerox copiers, photovoltaic cells and large area displays.

The basic properties of the semiconductors mainly depend upon the energy band structure for their operation [1,2]. Every semiconductor consists of a forbidden energy gap in which no energy levels can exist and above & below the energy gap there exist two energy bands. The upper band is known as conduction band while the lower band is known as valance band. The difference between these two bands is known as energy band gap $E_g$ a quite important factor for semiconductors.

There are two types of semiconductors

(i) Direct band gap semiconductors

(ii) Indirect band gap semiconductors,

This classification depends upon the corresponding positions of conduction band and valance band in K-space (Fig.1.1). When the conduction band minimum and the valance band maximum are located at the same K (wave vector) value = 0 then this type is known as direct band gap semiconductors. In this case there will be no change in momentum of photon in the transition from valance band to conduction band. Almost all the semiconductors of the group II - VI are direct band gap type semiconductors. But if there are a difference in the K-
Fig. 1.1 Details of band edges in semiconductors with Diamond, Zincblende, and Wurtzite structures

Fig. 1.2 Energy band diagram of a p-n junction
values of valance and conduction band then these are indirect band gap semiconductors. Any transition from valance band to the conduction band for different K-values involves a photon of light momentum. Some examples of indirect band gap semiconductors are Si, Ge, Al etc. The fact of direct and indirect band gap is a deciding factor for devices.

1.2 Semiconductor Junctions:

When a p-type semiconductor is contacted with n type semiconductor, electrons from n side of the contact diffuse into p side due to large number of electrons in n side. In p region, they recombine with free holes. As this process goes on, p region becomes negatively charged and n region positively charged. A dynamic equilibrium exists when a potential differences stops the further motion of the majority charge carriers.

A space charge is created in n and p regions both. The Fermi levels of n and p-type semiconductors become equal at the equilibrium. Fig. 1.2 shows the energy band diagram of a p–n junction.

When n type semiconductor is contacted with a metal having higher work function than that of semiconductor, the electrons which come due to ionization of donor levels, flow into the metal until the Fermi levels of metal and semiconductor become equal. In this process, the surface of the semiconductor becomes positively charged due to depletion of electrons.

The contact of p-type semiconductor with a metal having lower work function than that of semiconductor also makes a barrier where a negative space charge region is created in the semiconductor which stops the flow of holes. Fig.
1.3 shows the energy band diagram of such a barrier, which is also known as schottky barrier.

1.3 Photovoltaic Effect In Semiconductors:

As discussed above, a semiconductor can have an internal electric field due to potential barrier in p – n junction or in schottky barrier. When light photons of energy more than the band gap is shown on these devices, electron and hole pair are generated. These electrons and holes can be separated by internal electric field present in p – n junction or in schottky barrier. In p – n junction, light generated electrons diffuse into the n region and holes diffuse in p region and the barrier thus reduces. A current therefore can flow in a p–n junction when light is shown on this device. The lowering of the barrier represents the photovoltage across the junction. This phenomenon is known as photovoltaic effect. Separation of charge in semiconductor is equivalent to the separation of charge produced in a battery by chemical means. Semiconductor junctions can therefore be used to make solar cells as electrical energy can be obtained by shining sun light on these devices.

1.4 Hall Effect In Semiconductors:

When a magnetic field is applied at right angles to a conductor carrying a current, a voltage is developed across the metal in a direction perpendicular to the direction of current and magnetic field both. This phenomena has been observed in semiconductor.

Also, in n-type semiconductor, electrons are the majority charge carriers so hall coefficient is negative. On the other hand, in p type semiconductor, holes
Fig. 1.3(a) Energy band diagram of a Schottky barrier using p type semiconductor.

Fig. 1.3(b) Energy band diagram of a Schottky barrier using n type semiconductor.
are the majority carriers and Hall coefficient is said to be positive. In intrinsic semiconductor, Hall coefficient is very small. Hall voltage in these semiconductors is only due to different mobility of electrons and holes.

In general, for crystalline semiconductor, the sign of the Hall voltage is used to determine whether a semiconductor is p-type, n-type or the sign of Hall coefficient is opposite to what is expected from the nature of the majority charge carriers.

1.5 Crystalline Semiconductors:

Crystalline semiconductors are known for a long time and the theory of these semiconductors is also well established using the concepts of long range order in crystals. Since the generation of charge carriers can be controlled by temperature, light, high fields and impurities, semiconductors are most suitable for various kinds of solid state devices. The crystalline semiconductor are being used in making p-n junction diodes, schottky diodes, transistors, thyristers, field effects transistors, photodiodes, solar cells, high energy particles detectors and many more devices. Many works [3-5] have discussed the details of these devices.

1.6 Properties of Crystalline Semiconductors:

By semiconductor we mean a substance which has conductivity in between that of a conductor and an insulator. The distinction between an insulator and semiconductor is difficult to draw. However, normally a substance having conductivity less than $10^{-14}$ ohm$^{-1}$ cm$^{-1}$ does not fall under the category of semiconductor. The distinction between metal and semiconductor is quite sharp.
not by the conductivity range but by the temperature coefficient of resistivity which is positive in case of metals and negative for semiconductors. According to the band of theory of solids, the properties of semiconductors are described in terms of valence band, conduction band and forbidden gap.

The electrons in an isolated atom have the discrete energy levels. A solid contains a large number of atoms arranged in a lattice at a very small distance. The energy bands in a solid are produced due to spread of atomic energy levels. The band in which available states are occupied by valence electrons is known as valence band. On the other hand in conduction band, available states are occupied by electron, which can participate in electrical conduction. In semiconductors, these bands are separated by forbidden band. The energy difference between the highest filled valence band and the lowest empty conduction band is known as the band gap.

At absolute zero of temperature, the valence band of a semiconductor is completely filled and conduction band is completely empty. Due to thermal energy at any temperature other than absolute zero, a number of electrons become free. In terms of bands, one can say that electrons are excited to the conduction band and contribute to the conductivity. The empty state left in the valence band is known as a hole, which can also contribute to the conduction process. The conductivity of a semiconductor therefore has two components as follows:

\[ \sigma = n e \mu_n + p e\mu_p \]  

\[ \text{........................................1.1} \]
Where \( n \) and \( p \) are the density of electrons and holes respectively. \( \mu_p \) and \( \mu_n \) are their respective mobilities.

When impurities are added to an intrinsic semiconductor, the conductivity increases by several orders of magnitude. The impurity levels in a semiconductor can be of donor type (n type) which donate electrons to conduction band or can be acceptor type (p type) which accept electrons from valence band.

When an electron comes from valence band to an acceptor level, a hole is produced in valence band, which can contribute to conductivity. Similarly, electrons which are donated to conduction band by donor levels contribute to the conductivity of the semiconductor which increases in both the cases.

It must be noted that the donor and acceptor states in a semiconductor are localized in space because the impurity atoms occupy certain atomic sites in the structure. Because of this, donor and acceptor states are frequently called localized states.

In addition to donor or acceptor states, other kinds of defects in semiconducting crystals can also be produced. Each type of defects has a definite energy and produced localized states at that energy. These localized states can act as traps for electrons or holes. When probability of capturing electrons and holes become equal, a localized state can act as a recombination center.

Generation and recombination of charge carriers are simultaneous in a semiconductor. In thermal equilibrium, equal number of like charges appear and
vanish per unit time. The conductivity of a semiconductor depends upon these equilibrium electron and hole densities.

When light of proper wavelength falls on the semiconductor, free charge carriers (electrons and holes) can be generated. These excess charge carriers disturb the steady states of the semiconductor. A new dynamic equilibrium is set up which has more number of electrons and holes as compared to thermally generated charge carriers. Due to these excess carriers, an excess conductivity in presence of light is observed which is known as photocconductivity.

If the absorption of photons produces \( N \) electron hole pairs per unit time, the increase in density of electrons and holes is given by

\[
\Delta n = n \tau_n \quad \text{and} \quad \Delta p = N \tau_p
\]  \hspace{1cm} \text{1.2}

Where \( \tau_n \) and \( \tau_p \) are the effective lifetime of access electrons and holes respectively.

Following equation (1.1), the excess conductivity can be written as

\[
\Delta \sigma = e \Delta n \mu_n + e \Delta p \mu_p
\]  \hspace{1cm} \text{1.3}

Substituting the values of \( \Delta n \) and \( \Delta p \) from equation (1.2) to equation (1.3), one gets

\[
\Delta \sigma = e N (\mu_n \tau_n + \mu_p \tau_p)
\]  \hspace{1cm} \text{1.4}

Equation (1.4) shows that photocconductivity depends upon the lifetime of excess charges carriers and mobility of these carriers. When a semiconductor contains a large number of traps, the lifetime of excess carriers become quite small.
observed photoconductivity is, therefore, negligible in a semiconductor having large number of traps.

The quantum statistic plays an important role in determining the number of electrons and holes in conduction and valence band respectively.

Detailed calculations show that the conductivity in intrinsic semiconductors is given by

\[ \sigma \propto \exp \left( -\frac{E_C - E_F}{kT} \right) \]  \hspace{1cm} \text{1.5}

Here \( k \) is the Boltzmann's constant, \( E_C \) is the energy at the bottom of the conduction band and \( E_F \) is known as the Fermi energy. At the absolute zero of temperature, \( f(E) = 1 \) for \( E < E_F \) and \( f(E) = 0 \) for \( E > E_F \) is the probability of a quantum state, at energy \( E \), to be occupied by electron.

In case of intrinsic semiconductor \( E_F \) lies almost in the middle of the band gap, i.e., \( E_F = \frac{E_C - E_V}{2} \). Here, \( E_V \) is the energy at the top of the conduction band. The conductivity can therefore be written as

\[ \sigma \propto \exp \left[ -\frac{E_C - E_V}{2kT} \right] \]  \hspace{1cm} \text{1.6}

Equation (1.6) shows that the \( \sigma \) vs \( 1/T \) curve should be a straight line for an intrinsic semiconductor. The slope of this curve can be used to calculate the band gap \( E_g \) ( = \( E_C - E_V \)).
1.7 Amorphous Semiconductors:

Before the nineteenth century, solids were known as amorphous if they had a formless fracture surface. With the discovery of x-ray and electron diffraction, it was found that the substances, which were amorphous by fractography, were also non-crystalline. Since then, the word amorphous is used to mean non-crystalline on any significant scale. Long range order (periodicity of atoms for a larger distance) is almost absent in amorphous materials. However, they may have short range order up to a few atomic distances.

The amorphous threshold switch, which is also known as the ovonic threshold switch, named after the inventor S. R. Ovshinsky whose landmark paper in 1968 sparked a new field of research in the 1970's and 1980's [6]. In 1950's, it was found that non-crystalline solids and liquids, which do not have periodic structure, could also behave as a semiconductor. A. F. Loffe and A. R. Regal suggested that electronic properties of these semiconductors originate from short-range order rather than long range order.[7]

The improved understanding of the amorphous state which came from these studies has revived and refreshed interest in traditional glasses, particularly those doped with rare earth transition metals, which have optoelectronic applications in, for example, fibre optical amplifiers, as well as for coloured glasses. Organic is another research area which benefits from the insights gained from disordered materials. Solids, which are out of long-range order of crystallinity, are also termed as amorphous.
Amorphous substances are prepared by rapid cooling of the melt by condensing vapours on a substrate (thin films). In both the cases, due to rapid cooling, some of the bonds are not formed. These broken bonds are known as dangling bonds. Apart from the dangling bonds, some other kind of defects can also be created during the preparation of thin films. The properties of amorphous substances, therefore, depend strongly on preparation condition and results differ from one laboratory to other laboratory. It is very difficult to draw any conclusion unless a lot of experimental data is available. The properties of glasses are relatively more reproducible in the thin films.

Amorphous substances pose great problems to theoretical physicists also as the mathematical simplicity of the periodic structure does not exist in these materials. In these cases, the mathematics becomes so complex that it is very difficult to draw any conclusion from the calculations. This is the reason why our knowledge is poor in case of amorphous substances as compared to crystals. The mankind knows the fact of transparency for the last 10,000 years but the theoretical explanation of this transparency does not yet exist in the scientific literature.

Amorphous substances do not show sharp lines in bragg diffraction pattern unlike crystalline substances. A hole is generally observed in these materials.

Amorphous semiconductors do not have long range ordering of their constituent atoms. The array of equilibrium atomic positions is strongly disordered. It was long believed that the amorphous materials couldn't behave as
semiconductors. B. T. Kolomicts is the first person who started working on glasses containing one or more chalcogenide element (S, Se and Te)[1]. These glasses have larger properties, instead of conventional sixth group element, which was used to prepare glasses. It was found that these glasses behave similar to intensive crystal semiconductor. It was believed that these semiconductor are of no use because these semiconductor could not be constructed like n or p-type semiconductor by doping with V and VI group elements of the periodic table. Therefore one can classify the semiconductors only in two categories i.e. crystalline and non-crystalline. Chalcogenide glass, is the another name of non-crystalline semiconductors.

For an amorphous solid, essential aspect with which its structure differ with respect to that of crystalline solid is the absence long range order. There is no translation periodicity. The lack of long-range order in glasses implies randomness at large separations, the atomic-scale structure is highly nonrandom for a few interatomic distance about any given atom. Short-range order is very much in evidence in the structure of amorphous solids. Non crystalline solids, which are produced by melting and cooling process, are generally referred to as glass. Non crystalline solids made by non-conventional methods such as vapor deposition Sol-gel and solid state amorphization processes are sometimes referred to as glass and other times as amorphous solids. The lack of long-range order makes these materials very hard to extract structural information from the diffraction experiments. Many important amorphous solids are representable by disconnected covalent graph that is they are molecular solids. Molecular solids
are characterized by the coexistence of strong (primarily covalent) and weak (intermolecular, primarily 'Van der waals) forces, with the attendant appearance of cohesive atomic groupings.

For a long time it was thought that only a relatively restricted number of materials could be prepared in the form amorphous solids, and it was common to refer to these "special" substances (e.g. oxide glasses and organic polymers) as "glass forming solids". This notation was wrong and it is now realised that "glass forming ability" is almost a universal property of condensable matter. B. T. Kolomiets and his associates in the USSR first tried other VI group elements (S. Se. and Te) in place of conventional element 'O' which was used to prepare oxide glasses. They found that glasses prepared using one or more chalcogen elements (S. Se and Te) showed the semiconducting properties. Most of the chalcogenide glasses materials contain one or more of the chalcogen elements of the VI column of the periodic table such as sulfur, selenium and tellurium. An extensive research on amorphous semiconductors started when S. R. Ovshinsky detailing the various types of switching phenomena that characterized a large class amorphous solid, and the subsequent publicity describing many potential applications for these phenomena [3-5]. He also demonstrated the use of chalcogenide thin films for computer memory. A further interest in these semiconductors arose when W.E. Spear and P.G. LeComber at the University of Dundee. U.K. 1975, developed a technology to produce n and p-type amorphous silicon similar to their crystalline counterpart [8]. Since then, this material is being utilized in various solid state devices.
In many amorphous materials it is possible to control the short-range order parameter. The short-range structure can be made quite different from that in crystalline state of that substance. The structures therefore become a new variable by which the properties can be changed drastically in amorphous materials.

Amorphous state can easily be obtained by rapid cooling of the melt or by evaporating the materials in vacuum. By electroplating and by gas discharge also, one can make amorphous films. The preparation of amorphous substance is, therefore, much easier than growing single crystals. This feature of amorphous materials makes them suitable for making devices for commercial purposes at a cheaper rate than crystalline ones.

A large number of defects are introduced in crystalline substances when they are irradiated with high-energy particles. The properties of the crystalline substances thus change drastically after irradiation. On the other hand, amorphous substances do not have such drastic changes as they are already in disordered state. This feature of amorphous substances makes them suitable for space applications.

Long range order is almost absent in amorphous semiconductor, though they can have short range order up to a few atomic dimensions. The most important elements, which preserve short-range character, are silicon and germanium from group IV, arsenic, antimony and bismuth from group V and sulfur, selenium and tellurium from group VI of the periodic table. Elements from other groups may also be present but usually as a minority constituent.
Amorphous semiconductors may be single elements such as bulk selenium, tellurium or thin films of silicon and germanium; they may be compounds such as arsenic tritelluride; or they may be multicomponent alloys that form bulk glasses over a broad range of compositions.

Amorphous substance, unlike crystalline ones, does not have a sharp melting point. The transition from solid state to liquid state takes place within a finite time interval known as softening time.

Amorphous substances are isotropic, i.e. the properties do not depend upon the direction of measurement. Crystals are well known for their an isotropic nature where properties in different directions differ considerably.

Unlike crystalline substances, amorphous substances can exist in metastable structural states. New compositions and mixtures can therefore be prepared which may exceed the limits of thermodynamic equilibrium.

1.8 Properties In Amorphous Semiconductors:

The mechanism of transport of charge carriers in amorphous semiconductors has been the subject of intensive theoretical and experimental investigation for the last few years. These studies have been stimulated by the attractive possibilities of using the structural disorder in amorphous materials for the development of the better, cheaper and more reliable solid states devices, such as switching and memory devices, photosensors, imaging devices etc.

It has long been believed that the chalcogenide glasses show the p-type conduction only and that the control of the conduction type is impossible by doping technique since the valence of doped atoms is always satisfied in the
glasses. According to the band model of amorphous semiconductors developed by Mott. Et. Al. [9,10] and Kastner et. Al. [11] the above situation is explained by the pinning of Fermi energy due to the equilibrium between negatively D and positively, D'charged dangling bonds.

In view of electricity metals are good conductors while non-metals are insulators. The materials, having conductivity in between $10^{-6} - 10^4 \Omega^{-1} \text{cm}^{-1}$ are metals, $<10^{-6} \Omega^{-1} \text{cm}^{-1}$ are insulators $10^4 - 10^{10} \Omega^{-1} \text{cm}^{-1}$ are semiconductors. Metals have positive temperature coefficient of resistance while semiconductors have negative temperature coefficient of resistance. Semiconductors are very much sensitive to the presence of light and the variation of temperature. Semiconductors may be characterized by their structure, energy effective mass and carrier mobility. The properties may be altered by impurity doping [12].

Materials may be classified as crystalline and non-crystalline solids. If the atoms are periodically arranged in a repetitive mode then it is crystalline and if there no such arrangement then it is non-crystalline. Crystalline solids may be further divided in single crystal and poly-crystals. In single crystal there is only one crystal in entire solid while the polycrystalline materials are made up of grains, which are highly ordered crystalline regions of irregular size and orientation. Solids, which are out of long range order or crystallinity is known as amorphous. A large number of properties of the materials depend on the structure of crystals and on the electron states within the crystals. The properties of amorphous solids depend upon the preparation techniques. Except some examples these are unstable in reference of crystalline materials. Figure (1.4)
Fig. 1.4 Some Common Structures of Semiconductors

(a) Diamond structure
(b) Zinc blende structure
shows the crystal structures. Silicon and Germanium are of diamond structure, the II-VI group materials are of complicated structure due to the tendency of these to crystallize in a various polymorphic modification: II-VI compounds are either of zinblende structure or of hexagonal structure [13,14].

To have the knowledge about the band structure (which basically depends upon the crystal structure) one must study the optical properties [15,16,17]. When a light beam is incident on any semiconductor material, some part of the beam undergoes reflection, some passes through (transmission) and the material absorbs rest part. Interaction between photons and electrons takes place as well as between photons and the crystal lattice.

If the photons having energy \( hv (hv > E_g) \) there exists inter band optical transitions but photons of energy \( hv (hv > E_g) \) excitation transitions or the transitions between bands and doping levels can exists.

A lot of research work is going on in the area of amorphous and liquid semiconductors and there is a hope that very soon these semiconductors will overtake their crystalline counterpart.

1.8.a DC And AC Conductivity:

A dc and ac conductivity vary from sample to sample and results are sometimes highly intriguing. However, generally it is observed that dc conductivity \( (\sigma_{dc}) \) increases with temperature, similar to intrinsic crystalline semiconductors, in high temperature region (150 k and above). Single activation
energy has been observed from the slope of $\ln \sigma_{dc} \text{ vs } 1/T$ curve in the above temperature range.

At lower temperatures (below 150 k) $\sigma_{dc}$ shows variable range hopping type conduction as suggested by Mott and Davis [18] considering the localized states near Fermi level. According to these authors, $\sigma_{dc}$ due to this process is given by

$$\sigma_{dc} \propto \exp \left[ -\frac{T_0}{T} \right]$$

Where $T_0$ depends upon the density of localized states near Fermi level. This type of conduction is observed in various types of amorphous semiconductors. However, the chalcogenide glasses do not show this type of conduction. The reason of this discrepancy has been associated with the paired defect states in chalcogenide glasses. Unlike other amorphous semiconductors they do not have unpaired electron states.

AC conductivity is observed in amorphous semiconductors including chalcogenide glasses. AC conductivity ($\sigma_{ac}$) shows almost linear variation with angular frequency ($\omega$). One therefore writes

$$\sigma_{ac} \propto \omega^2$$

Where $s$ is found to have values from 0.8 to 1.0 for various amorphous semiconductors. AC conductivity is found weakly temperature dependent at low temperatures. At very high frequencies in low temperature range, $\sigma_{ac}$ which is explained due to contact effects.
In amorphous semiconductors also, $\sigma_{ac}$ is explained assuming the hopping conduction in localized states in the band tails and/or near Fermi level.

1.8.b Photoconductivity:

Photoconductivity is observed in amorphous semiconductors similar to crystalline ones. Photoconductivity increases with intensity ($F$) as follows

$$\sigma_{ph} \propto F^\gamma$$

1.8

where $\gamma$ varies between 0.5 and 1 depending upon the temperature and intensity range. In chalcogenide glasses, photoconductivity is weakly temperature dependent at very low temperatures. As the temperature increases, $\sigma_{ph}$ increases exponentially with activation energy of about 0.2 eV. A maximum in photoconductivity is observed near 250 K in most of these glasses.

Wavelength dependence of $\sigma_{ph}$ is also studied for various types of amorphous semiconductors. Light having energy smaller than the optical gap is also found to have photoconductivity. This is explained by assuming the presence of localized states in the gap of amorphous semiconductors.

Due to the presence of localized states in the gap, the transient photoconductivity in amorphous semiconductors has decay time in minutes in some of the cases. Photoconductivity measurements have been utilized to get information regarding the localized states, recombination mechanism and to find out the lifetime of the excess carriers.
1.8.c Optical Absorption:

Similar to crystalline semiconductors, optical absorption edge is observed in amorphous semiconductors also. The edge is, of course, not very sharp due to the localized states present in the band gap. As described earlier, these localized states near the band edge arise due to the absence of long-range order in these semiconductors.

1.8.d Mobility:

Mobility of electrons and holes in amorphous semiconductor is much less as compared to crystalline semiconductors. This is expected in these semiconductors as they do not have the periodicity of crystals. Due to small mobility of charge carriers, the resistivity of these semiconductors is much larger as compared to their crystalline counterpart.

1.8.e Hall Effect And Thermoelectric Power:

In crystalline semiconductors, an n type sample shows negative thermoelectric power and also negative hall coefficient. Similarly, p type materials shows positive sign in both the cases.

However, in case of amorphous semiconductors, the sign of the hall effect is always opposite to that obtained from thermoelectric power: n typed doped samples show a positive Hall coefficient and p type doped samples a negative one. On crystallisation, the Hall coefficient has the sign of the carrier. This discrepancy is explained by assuming the dominant transport due to hopping in localized states. In hopping conduction, the sign of the transfer integral and the
number of sites necessary to make a closed path. The Hall voltage, therefore, may be positive even when electrons are the majority carriers.

**1.8.f Electron Spin Resonance:**

Amorphous semiconductors show electron spin resonance (ESR) indicating the presence of free spins. This is probably because of dangling bonds, which are more likely in amorphous films. In case of thin films, not enough time for bonding is available before condensing on the cold substrate from vapour phase. Chalcogenide glasses do not show electron spin resonance under ordinary conditions. It is due to the presence of paired defect states which is quite favourable in these glasses as compared to unpaired defects.

**1.8.g Paramagnetic Behaviour:**

Crystalline semiconductors normally show diamagnetic behaviour. Amorphous semiconductors, on the other hand, show paramagnetic behaviour due to the presence of free spins because of dangling bonds. However, as expected, paramagnetic behaviour is not observed in chalcogenide glasses.

**1.8.i Doping:**

In the beginning, amorphous semiconductors could not be doped. It was thought that impurity atoms could satisfy their valence requirement by adjusting the nearest neighbour distance in an amorphous semiconductor. However, in 1975, Spear and Lecomber [8] could dope amorphous silicon, which was prepared by, glow discharge of silane gas. These workers also measured density of localized states in the gap by field effect technique and found that this density
near Fermi level was three to four orders of magnitude smaller in this materials as compared to evaporated silicon. The question why amorphous silicon prepared by glow discharge of silane gas gives different properties than evaporated/ sputtered amorphous silicon was answered when Fritzsche et.al.[19] showed that these films contain hydrogen up to 10 atomic percent. On heating, hydrogen comes out of the films at round $400^\circ\text{C}$ and then these films are as bad as prepared by evaporation or sputtering. Using I–R spectroscopy, it was found that in good quality films prepared at $300^\circ\text{C}$, hydrogen is attached to silicon as monohydride (see fig. 1.5).

This shows that hydrogen helps in removing the dangling bonds inside the materials and thus reducing the density of localized states near Fermi level. Since these films contain a large amount of hydrogen, hydrogenated amorphous silicon is known as an alloy of silicon and hydrogen (a-Si : H). This materials is alternatively produced by sputtering silicon in the presence of hydrogen [20]. Post hydrogenation of sputtered amorphous silicon also gives similar properties [21]. Recently, ion beam sputtering [22] and homogeneous chemical vapour deposition [25] have also been used to produced good quality a – Si : H films.

Hydrogenation of amorphous silicon films helps in the reduction of the density of localized states near Fermi level. This is the reason why these materials could be doped n or p-type.

Hydrogenation of chalcogenide glasses was also tried by H. Fritzsche and his co-workers [24] but the success could not be achieved in reducing the number of localized states and hence doping could not be achieved. S.R.
a - Si: H
Curve a: $T_S = 300\,K$
Curve b: $T_S = 580\,K$

Peak
1: Si-H$_2$ Stretching
2: Si-H$_2$ Stretching
3: Si-O-Si
4: Si-H$_2$ Bending
5: (Si-H$_2$)$_n$
6: Wagging

Fig. 1.5
Ovshinsky [25], however could change the conductivity of these glasses by 10 orders of magnitude by chemical modification of a particular glass. This modification was achieved by sputtering the materials at low temperatures. If one mix the same amount of impurity in the liquid phase the significant change in conductivity could not be achieved.

Recently, it has been reported [26] that p type Ge – Se – Bi glass transforms to n type if Bi percentage is changed to more than 7 atomic percent. This opens a possibility of changing the density of localized states in the gap even by mixing the impurities in the liquid phase. Efforts are being made to prepare new compositions where p to n type changes could be made very sharp.

1.8 j Switching:

Amorphous semiconductors show reversible switching in which sample goes from high resistance state (OFF State) to very small resistance state (ON State) when voltage applied across them exceeds a particular value called threshold voltage. Two types of switching are observed in these semiconductors, namely, threshold and memory. In threshold switching, sample comes back in its original state when current is reduced to a value less than the holding current. On the other hand, in the case of a memory switch, the system remains in the ON state when the current reduces to zero or is reversed. A memory switch, however, can be made to come back in its original state (OFF State) after applying a high current pulse for a short time. The memory switch retains its on states only if it is kept in that state for a certain period of time called Lock on time.
If sufficient time is not provided, a memory switch also behaves as a threshold switch. This lock on time is of the order of $10^{-6}$ sec.

It is observed that a current channel is formed when switching takes place. In case of memory switching this channel is crystallized. The lock on time is the time required for this crystallization. Those materials which have large crystallization tendency normally show memory switching. When a high current pulse passes through this crystallized region, sufficient energy is provided to the system to break the bonds and allow sufficient diffusion of the atoms forming the crystallized materials. The subsequent rapid cooling of the materials changes this crystallized channel to amorphous state.

The threshold voltage is found to depend upon temperature and resistivity of the materials independent of the type of switching displayed by these materials. The power required for switching is also found to be the same for various types of materials having threshold and memory switching. These results show that thermal effects are important in switching phenomena. The temperature near the electrodes is also observed to be quite high at the time of switching.

Two main models have been suggested for the switching in amorphous semiconductors. In the thermal model, the physical process is joule heating, which raises the temperature inside the semiconductor. The resulting increase in conductivity allows more current flow. A new stationary state is established when the heat generated away from the current filament equals the Joule heat generated in that region. In the electronic model of switching the high current is
assumed to be due to high field conducting in these semiconductors. It is not easy to distinguish which of the phenomena is responsible for switching. An electro thermal model is, therefore, considered more appropriate for switching where thermal and electronic effects are simultaneous. The only problem is to find out which one is predominant in a particular material.

It is normally agreed that in the samples having large conductivity where large heating is possible, thermal effects are more dominant. In thin films or in samples having small conductivity, electronic process are dominant.

1.9 Distinction Between Crystalline And Amorphous Semiconductors:

The word 'amorphous' is used to mean non-crystalline on any significant scale, as the periodicity of atoms does not hold for long distance in amorphous materials. The X-ray or electron diffraction patterns therefore do not show sharp lines unlike crystalline substances.

Given below are some of the special characteristics of amorphous semiconductors, which distinguish crystalline counterparts:

(i) Thermodynamic equilibrium does not exist in these semiconductors. They are stable because the thermal energy at room temperature is not sufficient to overcome the potential barrier to change a semiconductor from amorphous to crystalline state. Obviously when, one heat amorphous semiconductors to higher temperatures, they show a transition form amorphous to crystalline state with a release of considerable energy. As thermodynamic equilibrium is not required, amorphous semiconductors may exist in several different structural states. Like
alloys, various compositions can be made of these semiconductors using two or more elements. These semiconductors are therefore known as tailor-made materials because changing the composition can change the properties of these materials.

(ii) Amorphous semiconductors can be change their structure by external means in such a way that reversible changes may occur in them. The structure becomes a new variable by which properties of these semiconductors can be changed drastically.

(iii) A crystalline semiconductor, when irradiated with high-energy particles, tends towards non-crystalline state. The properties of these materials change drastically on this action. On the other hand radiation do not affects amorphous semiconductors much as they are already in non-crystalline state. This is probably the main reason why amorphous semiconductors are explored with great enthusiasm so that they could be used in space applications where crystalline devices produce noise due to radiation.

(iv) The technology of preparing amorphous semiconductors is much easier and therefore less costly than growing single crystals for crystalline devices. Amorphous semiconductors can easily be prepared in the form of thin films by vacuum evaporation or sputtering. Due to their thin film form, integrated circuits can easily be fabricated.

All these simplifications have made amorphous semiconductors most suitable for cheaper semi conducting technology.
1.10 Classifications of Amorphous Semiconductors:

It is difficult to classify amorphous semiconductors as they have a wide spectrum having different properties. However, Amorphous semiconductors are most easily classified in exactly the same manner, as are crystalline semiconductors i.e. by the type of chemical bonding that is primarily responsible for cohesive energy of materials. In crystalline solids, we considered five major classes of materials such as ionic, covalent, metallic, Van der Walls and hydrogen bonded materials. This classification scheme can also be used for amorphous solids. Amorphous metal does exist, and appear to have approximately the same conductivity as the corresponding crystalline materials. The effects of long-range disorder on the electronic properties of solids are quantitative rather than qualitative. Van der walls and hydrogen – bonded solids generally have low cohesive energies and thus low melting temperatures. Thus the field of amorphous semiconductor can be broken down into ionic and covalent materials. The ionic materials, which have studied most, are the halide and oxide glasses, particularly the transition metal oxide glasses. Recently, simpler amorphous solids, such as V₂O₅ and NiO, have been prepared by rf-sputtering techniques. Being primarily ionic, the composition of these materials cannot be made to vary over a wide range, and the pure materials have just positional disorder. On the other hand, in the transition–metal oxides, the presence of impurities usually create two different valence states. For example, introduction of P₂O₅ into V₂O₅ produces V⁴⁺ ions as well as V⁵⁻ ions. Thus, these materials can be said to posses some degree of electronic disorder. Further
more, the unsaturated transition metal ions generally contribute some spin, disorder.

It will be convenient to further break the covalent amorphous semiconductors into two classes, by separating out the purely elemental materials. This group, which is perfectly covalently bonded of course includes Si, Ge, S, Te and Se among others elements. Since all atoms are necessarily the same, these materials possess only positional disorder. Thus, they are the simplest amorphous semiconductors to investigate theoretically. The remaining covalent materials include such binary materials as As₂Se₃ and GeTe, as well as the multicomponent boride, arsenide and chalcogen glasses. Being primarily covalent, there is nothing magic about the chemical composition. As₂Se₃ nominally contains 40% As and 60% Se but there is no reason why we cannot make an alloy of say 45% As and 55% Se or any other proportion we desire. Since the material is amorphous, we are not tied to any crystalline structure, and thus defects dangling bonds and antistructure are not the problems. Similarly, we can combine As, Se, Ge and Te and can produce, for example, As₃₁Se₂₁Ge₃₀Te₁₈ which is a chalcogenide glass. The significance of this is that the covalent amorphous semiconductors always possess compositional as well as positional disorder. As we shall see, the profound effects of this point disorder on the electronic band structure are responsible for the distinctive properties of these glasses, and justifies their separation from the class of elemental amorphous semiconductors.
As in crystalline solids, many mixed ionic covalent amorphous materials exist and these have to be analyzed carefully. The similarities in short-range order and bond length between corresponding crystalline and amorphous solids implies that the atomic electro-negativity is independent of the nature of material. We can use these properties to estimate the average fractional iconicity of a given alloy.

The structure of all non-crystalline semiconductors lack long-range order and far way from a site seems to be randomly distributed but short-range does exist. The state of material may be regarded as a supercooled liquid. Chalcogenide glasses material heat to melt in the form of a liquid and at the some instant freeze the position of every atom by quenching. Even in this freezed position they retain short-range order and the position of nearest neighbour remains nearly same. For instant in non-crystalline Germanium, each atom is surrounded by four nearest neighbour. This can be arranged in two different ways one that the atom at the opex of the tetrahedron and the other at the center of new tetrahedron. In non-crystalline germanium both arrangements occurs with essentially equal likely hood and it leads to disorder in second nearest neighbours. As the process is extended further and further away for original atom, the numbers of the possible position multiply rapidly resulting in complex disorder at long range. This type of disorder is termed as positional disorder and prevails in all non-crystalline elemental semiconductors like germanium, silicon, selenium and tellurium.
In binary non-crystalline semiconductors besides positional disorder, compositional disorder also exists. For example in non-crystalline Ge or Te the structure becomes such that there becomes equal probability of finding Ge or Te atoms at any position. This is compositional disorder and exists in other binary non-crystalline semiconductors like As$_2$S$_3$ and others.

In multi-component non-crystalline semiconductor like As$_{20}$Se$_{30}$Ge$_{40}$Te$_{10}$ there is equal or even more compositional disorder but four nearest neighbours forming the familiar tetrahedral covalent bonding surround every Ge atom.

### 1.11 Electronic Models Of Chalcogenide Glasses:

The carriers in amorphous systems are strongly affected by the randomness of atomic arrangement due to the absence of long-range order. Mott$^6$ has argued that the spatial fluctuation in the potential, caused by the configurational disorder in amorphous materials may lead to the formation of localized states, the valence and conduction bands do not have sharp cut off but have a tail above and below the normal band. The extent of these tailing is expected to be enhanced in alloys which contain compositional disorder in addition to positional disorder.

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

Cohen, Fritzsche and Ovshinsky first suggested that in the case of disordered covalent alloys, such as chalcogenide glasses, the valence and
conduction band tails overlap each other close to the center of the forbidden gap. The mobility of the carriers has finite value in high density states but it decreases abruptly in tail states (see Fig. 1.6). These boundaries are called mobility edges. The critical energies at mobility edges define a mobility gap.

Davis and Mott [27] proposed that there is a narrow band of compensated localized states, which pin the Fermi level between the two tails (See fig. 1.6). This model suggests that hopping conduction can take place in the localized states near the Fermi level.

Mott and his collaborators [28] further elaborated the model of gap states in chalcogenide glasses. They considered the states near Fermi level due to defects, e.g. dangling bonds. Two electrons are shared in a chemical bond between atoms. In some structural configuration, the atoms are not able to share the electrons and the bond is broken. This is called a dangling bond. A dangling bond is neutral ($D^0$) when occupied by a single electron. In some cases, dangling bond can attract an electron, and become negatively charged ($D^-$), or attract a hole and become positively charged ($D^+$). They based their model on the assumption that paired electron states are preferred in chalcogenide glasses.

In general it is accepted that the localized states in amorphous semiconductors do not correspond to a single energy but have an energy distribution. Various methods, e.g., field effect, space charge limited conduction, deep level transient spectroscopy, barrier capacitance measurement and thermally stimulated currents have been employed to study the localized states in amorphous semiconductors.
Fig. 1.6 Various models for amorphous semiconductors.
The most accepted model for the density of localized states assumes a continuous distribution of localized states having its minimum value near Fermi level. The density of localized states varies with energy on both sides of the Fermi level towards conduction and valence bands.

1.12 Properties of The Thin Films:

An independent and important branch of Physical science that has been developed continuously is the Physics of thin films. The name of thin film is not new in the field of science and technology however Bunsen and Grower obtained the thin film in 1852 by explosion of a current carrying metal wire, but it came to know 1864, when the first solid thin films was obtained by electrolysis. Thin films are used in so many devices such as solar cells, detectors, magnetic memory devices, bolometer, optoelectronics, interference filters, xeroradiography, reflection and anti reflection coating. The progress has also brought much confidence in the use of thin films for basic and applied research. Thin films studies have directly or indirectly advanced many new areas of research in solid state Physics and Chemistry, which are based on the phenomena uniquely characteristic of the thickness; geometry and structure of the films. Thin films have been extensively studied for over a century because of their potential, technical value and scientific curiosity. The study of thin surface films involves several fields of fundamental and practical importance. The film prepared by the use of semiconductors conducting materials is of the most importance in science and technology.
Films of semiconductors conducting materials are of great importance due to their wide use in various solid-state devices also. II- VI group compounds are widely used in solid-state devices such as infra-red detector, photovoltaic cells, nuclear radiation detectors and window for IR laser etc. These are the important semiconductors for opto-electronic devices. This group is much more important for photo-conductive and photo-electric devices [29].

The thin films of semiconductors conducting materials have covered a wide area of the field of technology and research. Now a days these films are the integral part of large number of devices. In modern technology one can control the physical properties of these films within the limits required for the use by the appropriate range of parameters like the deposition technique rate, substrate temperature and impurity etc. In last few years a lot of work has been done on A B semiconductors compound films. These compounds are simple binary compounds composed of elements belonging to the groups II & VI of the periodic table. Some of them form zincblende cubic crystals and are therefore directly analogous to the III-V compounds of the periodic table, but the others have the hexagonal wurtzite structure. These two crystal structures are closely related, both being made up of tetra-hedrally bonded. A variety of applications of A B semi-conducting compounds have been found in the field of micro-electronics, opto-electronics and automation. These applications depend upon the band gap and their nature, position of electron-hole traps in the energy gap, mobility of charge carriers and electron work functions etc.
1.13 Optical Absorption Edge In Chalcogenide Glasses:

Many crystalline semiconductors are opaque similar to the metals in the visible portion of the light. However, they are transparent in the infrared region. The light photon is observed only when the energy of the light exceeds the energy of the band gap. The transmission through the semiconductor reduces to zero sharply at a particular energy. This is known as optical gap of the semiconductor. At higher energies than the band gap, photon is able to excite an electron occupying a quantum state at the top of the valence band to the quantum state and at the bottom of the conduction band. The crystal thus appears opaque at these energies.

When the quantum states in the gap exist (donor or acceptor levels), transmission may show dips at lower energies also. If thermal energy is kept low (at low temperatures) transmission measurements may be able to determine the energies of donor or acceptor states.

1.14 Uses Of Chalcogenide Glasses:

The fact that amorphous semiconductors can be prepared in thin film form which requires simple technology than growing single crystals has made these materials more interesting from device point of view.

Chalcogenide glasses and hydrogenated amorphous silicon have been used for various solid state devices. Given below are some of the uses of these materials.

Chalcogenide glasses are transparent in infrared region and are, therefore, used in infrared lenses. They are not influenced by micro-impurities
and moisture and are, therefore, used as a moisture proof coatings on various solid state devices.

The photo structural changes are also observed in these glasses. They can, therefore, be used in optical mass memories. These glasses are also found suitable for image converters and intensifiers, ultrasonic delay lines and phase contrast holograms.

Memory switching has found application in computer memories. S.R. Ovshinsky at Energy Conversion Devices Inc, USA, has developed a 1024 bit computer memory using chalcogenide glasses. These are commercially produced and are successfully used in computers.

Since threshold voltage depends upon temperature, the use of chalcogenide glasses in thermalswitch is also suggested. Due to high current capacity, such switches can be used in automobile engines and large power machines where temperature control is needed.

Chalcogenide thin films show photocontraction in which the volume of the substance changes and density becomes large in presence of Light. This property of chalcogenide glasses is being used in lithography.

Efforts are being made to dope these glasses and then they can be used for others solid state devices where n or p type semiconductors are required.

After the discovery of hydrogenated amorphous silicon which has much smaller density of localized states, Carlson and Wronski [30] first demonstrated that a – Si: H can be used for cheap solar energy conversion. They used a–Si: H Schottky barriers to produce solar cells and obtained an efficiency of about 5.5%.
Though the efficiency of a – Si: H cells were smaller than that obtained using crystalline silicon, continuous efforts was made to improve the efficiency. Recently, the efficiency of amorphous silicon solar cells has been increased to 12%.

(i) Amorphous silicon solar cells have been produced commercially [31] and are being used in pocket calculators, watches, radios, clocks etc. The process of fabrication of these cells is much simpler and cheaper as compared to crystalline solar cells. Industrialization is possible for these cells and therefore they have great potential for cheap solar energy conversion.

On the other hand, the sensitivity characteristics of a-Si:H solar cell exactly match with the spectral distribution of the fluorescent light. These cells are, therefore, as efficient in fluorescent light as in sunlight. This property of a-Si:H solar cells makes them suitable for consumer products, e.g. calculators, watches, radios and clocks.

To improve the quality of Chalcogenide glasses material various preparations conditions are changing continuously. Efficient doping in these films also being tried so that one can make p-n junction and other solid state devices equally good as are made using crystalline silicon. Transport properties, role of hydrogen, light induced effects and amorphous silicon super lattices are the main topics of recent research on these materials.

On chalcogenide glasses also, attempts are being made to dope these glasses and to make n or p-type semiconductors so that they could be used in devices similar to their crystalline counterparts. Various new alloy systems are
being explored to find out suitable material, which can be good photoconductor and have potential use in device applications.

Research on the theoretical side is also progressing but not much success has yet been made, as mathematical simplicity does not exist in these materials. Attempts are being made to extend the theories and models, which are already available for crystalline semiconductors. A lot of theoretical work is needed to explain many effects of amorphous semiconductors. Theoretical work is being done on the same amorphous semiconductors till date by many works.

B.T. Kolomiets and his associates in USSR first started working on glasses containing one or more chalcogen elements (S, Se and Te) in large proportions, instead of conventional six group elements, 'O' which was used to prepare glasses. They found that these glasses (known as chalcogenide glasses) behave similar to intrinsic crystalline semiconductors. These workers did not consider these semiconductors very interesting, as they could not make n- or p-type semiconductors by doping them with Vth or IIIrd group elements of the periodic table.

In 1968, S. R. Ovshinsky first observed reversible switching in chalcogenide glasses and reported two types of switching, namely threshold and memory. Since then, chalcogenide glasses are being studied in detail by physicists as well as by engineers. Over a span of about 15 years, various solid state devices using these glasses have been developed which include image converters and intensifiers, switching and memory devices continuous dynode electron multipliers, optical mass memories, phase contrast holograms, high
energy particle detectors, infrared lenses, ultrasonic delay lines and microfiche transparencies etc.

Other crystalline semiconductors e.g. Si and Ge were also made in the form of non-crystalline films by vacuum evaporation, sputtering, electrolytic deposition and gas discharge. Hydrogenated amorphous silicon is found most suitable for making p-n junctions, Schottky barriers and other solid state devices. This material is successfully being used for the cheap solar energy conversion.

Thermodynamic equilibrium does not exist in amorphous state. However, the thermal energy at room temperature is not sufficient to overcome the energy barriers to convert an amorphous substance into a crystalline one. When amorphous substance is heated to high temperatures, it tends towards its crystalline state with a considerable release of energy. An exothermic peak is, therefore, observed in differential thermal analysis at the temperatures where crystallization takes place.

Chalcogenide glasses are being successfully used in computer memory. These devices are being made AT Energy Conversion Devices, Inc, Troy, Michigan, USA. Si:H combination is successfully being used in solar cells. Industrialization of these cells has been done by Sanyo Company in Japan. This company is selling pocket calculators, Using amorphous silicon solar cells, for the last few years. Large scale power generation using mass produced solar cells is also being tried in various countries. Apart from the application in solar
cells, a-Si:H is also being used in other solid state devices similar to its crystalline counterpart.

The aim of the present thesis is to observe the optical properties of the thin films of the chalcogenide glasses. Various properties have been described qualitatively. Emphasis has been given to optical properties as these semiconductors are most suitable for electronic devices.

In introduction to the semiconducting properties of crystalline substances and to the amorphous state of a substance has been given in section 1.5 and 1.7 of this chapter. Sections 1.6 and 1.8 deal with the properties of crystalline and amorphous semiconductors respectively.