Chapter 1

An Introduction to Chalcogenide Glasses and the Selection of the Problem
Chapter-1

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1. Introduction:

1.1 Introduction:

Amorphous solids have been used as so called glasses with various modifications in our life since more than 2000 B.C., i.e., the earliest glass objects were beads, which have been found in Egypt, and glass was actually made in earlier Mesopotamia. However scientific investigations on amorphous solids only started in this century, particularly about sixty years ago. Only in 1950’s it was found that non-crystalline solids and liquids that do not have periodic structure might also behave as semiconductors. A. F. Joffe and A. R. Regel [1] suggested that electronic properties of these semiconductors originate from short-range order rather than long-range order.

Glasses are a subset of the broader group of amorphous materials: glasses are made by rapidly quenching a liquid from the melt, resulting in a structure with disorder “frozen in”. The disorder in atomic positions of glasses leads to emergent phenomena unknown in crystals. The properties of a large collection of atoms with disorder reveal features that are unique, important and useful. The obvious example is that electronic and vibrational states may be localized – confined to a compact volume of space. In crystals, all electronic or vibrational states are extended through space (though not necessarily uniformly) as a trivial consequence of Bloch’s theorem. Observables such as the electrical and thermal conductivity are sensitive to localized states, and produce physical properties very different from their crystalline counterparts.
Amorphous materials present a challenge and an opportunity to the condensed matter theorist. There is a zoo of interesting physical processes unique to these systems and important technological applications that could benefit from materials optimization and basic understanding.

In the last decades, the amorphous solid state has received more and more attention in the literature. The reasons are the fundamental scientific interest, as well as the potential applications. Already since the early 19th century there was glasses looked for, showing transparency in the infrared (IR) spectral region. The oxide glasses were found to be IR-transparent till 3-5 µm, while the heavy-metal oxides showed values up to 7-8 µm [2, 3]. Systematic research has been performed including combinations of elements from the VIth main group of the Periodic Table. In 1955, for the first time in the history of solid-state physics, B.T. Kolomiets and his associates in USSR used chalcogen elements (S, Se, Te), i.e., the elements of group VI B of the periodic table excluding oxygen to prepare glasses. In order to differentiate these glasses from the oxide glasses a special name ‘chalcogenide glasses’ was given to them or they were baptized as ‘chalcogenide glasses’. In this way chalcogenide glasses came into existence. The reason for this differentiation was historic as well as scientific [4].

Oxide glasses are generally insulators with large values of the band gap (~10 eV in the case of SiO₂) and are transparent solids known for their inertness and stability, whereas for their chalcogenide analogs (i.e. sulfides, selenides and tellurides) the gap is generally smaller (1 - 3 eV) and hence these materials are semiconductors. These glasses exhibit unexpected sensitivity to band gap light, leading to several novel photoinduced effects. As a result, a wide variety of changes can be induced in chalcogenide glasses by the absorption of photons of energy comparable to the optical band gap.
These glasses find application in number of commercial devices because of their unique features: quasistability, photoconductive properties, infrared transparency, and ionic conduction. Thus the field of physics of the chalcogenides grew with the support of the large variety of characteristic properties of the non-crystalline chalcogenides.

**General Characteristics of Solid State**

Under a given set of conditions of temperature and pressure, which of these would be the most stable state of a given substance depends upon the net effect of two opposing factors. Intermolecular forces tend to keep the molecules (or atoms or ions) closer, whereas thermal energy tends to keep them apart by making them move faster. At sufficiently low temperature, the thermal energy is low and intermolecular forces bring them so close that they cling to one another and occupy fixed positions. These can still oscillate about their mean positions and the substance exists in solid state. The following are the characteristic properties of the solid state:

- They have definite mass, volume and shape.
- Intermolecular distances are short.
- Intermolecular forces are strong.
- Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.
- They are incompressible and rigid.

**1.2 Amorphous and Crystalline Solids:**

Solids can be classified as crystalline or amorphous on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the
arrangement of constituent particles (atoms, molecules or ions) is ordered. It has long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids. An amorphous solid (Greek *amorphos* = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only short range order. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only. Such portions are scattered and in between the arrangement is disordered.

Crystalline solids have a sharp melting point. On the other hand, amorphous solids soften over a range of temperature and can be moulded and blown into various shapes. On heating they become crystalline at some temperature. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called pseudo solids or super cooled liquids.

Crystalline solids are anisotropic in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions. Since the arrangement of particles is different along different directions, the value of same physical property is found to be different along each direction. Amorphous solids on the other hand are isotropic in nature. It is because there is no long range order in them and arrangement is irregular along all the directions. Therefore, value of any physical property would be same along any direction.
Distinction Between Crystalline and Amorphous Solids

Fig. 1.1 shows the difference between crystalline and amorphous solids

**Crystalline Solids**

- Definite characteristic geometrical shape
- Melt at a sharp and characteristic temperature
- When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth
- They have a definite and characteristic heat of fusion
- Anisotropic in nature
- True solids
- Long range order

**Amorphous Solids**

- Irregular shape
- Gradually soften over a range of temperature
- When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
- They do not have definite heat of fusion
- Isotropic in nature
- Pseudo solids or super cooled liquids
- Only short range order.
Figure 1.1: Structure of (a) crystalline and (b) amorphous solids.
The band structure of amorphous materials is shown in Fig. 1.2. The absence of long range order in amorphous materials causes the randomness of atomic arrangement which strongly affects the carriers in these systems. Mott has argued that the spatial fluctuations in the potential, caused by the configurational disorder in amorphous materials may lead to the formation of states. A band gap may, however, exist in amorphous semiconductors due to short range order in them. Due to states, the valence and conduction bands do not have sharp cut off but have a tail above and below the normal band. If disorder is large these tails can overlap in the mobility gap. In some regions of the material, the electron in the valence band can have higher energies than the electrons in non-bonding states of conduction band in some other part of the material. In order to lower their energies, these electrons move from the valence band tail into the states in the conduction band tail. The empty valence states, so formed, give rise to a random distribution of localized positive charges and the occupied conduction band states develop an equal number of localized negative charges. These charged states, above and below the Fermi level, act as efficient trapping centers for electrons and holes. As a result, conductivity of amorphous semiconductors becomes less sensitive to doping as compared to its crystalline states.

1.3 Classification of Amorphous Semiconductors:

Amorphous semiconductors can be classified into different categories depending upon their physical and chemical properties, and techniques employed for their preparation. Thermodynamically, these materials are unstable and tend to relax with time towards a stable or metastable phase. A brief description of some of these categories is given below:
Figure 1.2: Band structure of amorphous material.

1.3.1 Covalent Amorphous Semiconductors:
The covalently bonded amorphous semiconductors can be subdivided into three different parts

1.3.1 (i) Tetrahedral Amorphous Semiconductors (TAS):
These are group IV and III-V semiconductors. Being metallic, above their melting point they can be prepared either by thin film deposition or by
amorphisation. They cannot be prepared by quenching the melt, because the melt has a structure characterized by higher co-ordination number.

1.3.1 (ii) Tetrahedral Glasses (TG):

They may be represented by the general formula $A^{II}B^{IV}C_2^V$, where the suffix gives the group of the periodic Table. The interesting feature of the tetrahedral glasses is that although the Fermi level lies always near the middle of the gap, still some of them are n-type or p-type materials [5].

1.3.1 (iii) Chalcogenide Glasses (Lone Pair semiconductors):

Chalcogenide glasses are formed from the group VI elements of the periodic table such as Sulphur (S), Selenium (Se) or Tellurium (Te) (also called chalcogens). Like Silicon (Si), the best known and most widely used in IC technology, chalcogenides as Germanium Selenide (GeSe) and Arsenic Sulphide (As$_2$S$_3$) are poor conductors of electricity, unless some impurities are added to these materials. This process of impurity addition is called doping. However unlike Silicon, which has to be manufactured in an extremely pure crystalline state for use in most electronic devices, chalcogenide glasses do not have extended order in the arrangement of their atoms. This means that they can be deposited very easily, using any of number of well-known thin film manufacturing techniques, and are not nearly as susceptible to the presence of contamination or defects in their structure as Silicon. Chalcogenides are also known as Lone Pair semiconductors, because of their distinct feature of having two non-bonding p-orbitals of the group VI chalcogen in two fold coordination, which accounts for many of their unique properties.

1.3.2 Ionic Solids (Semiconducting Oxide Glasses):

The ionic solids are inorganic glasses consisting of mixtures of silicates with strong ionic bonds. These glasses are usually good insulators but can be
made semiconducting by the addition of the transition metal ions in different valance states. The conduction process then proceeds via a charge exchange among the valance transition metal ions. These glasses are widely used in everyday applications like window glasses, glass tubing and optical instruments. These include halide and oxide glasses, vanadium phosphate and iron phosphate glasses [6-8].

1.3.3 Metallic Amorphous Solids:

The most widely used metallic solids are, metglass alloys which consist of base metals such as Fe, Ni, Al, Co, Mn, Cr and Cu together with inexpensive metalloids B, C, Si, P, N, Ge and As. Metglass alloys with Fe, Ni and Co are amorphous solids. In addition, there are rare earth-transition metal amorphous alloys like GdCo, GdFe, GdTbFe which have good magnetic properties. Because of high quenching rate required, these materials are prepared by melt-spinning and sputtering [9]. These materials are found to have superior magnetic properties than their crystalline counterparts [10].

1.4 Band Models for Amorphous Semiconductors:

A model for the electronic structure of a material is needed to properly interpret the experimental data of electrical transport properties. However most of the existing theoretical work on the electronic band structure of solids has focused on crystalline materials. The band model, which has been proved helpful in explaining the behaviour of crystalline materials, is not directly applicable to the highly disordered materials. However, the band models used to explain the behaviour of amorphous materials assume a band of extended states along with the localized states. The periodic nature and symmetrical properties of crystalline materials makes it much easier to examine the band structures of these
materials theoretically. Because of absence of long range order in amorphous materials, it is not possible to have single band model which explains all the properties of amorphous materials. The band models used to explain the behaviour of amorphous materials assume a band of extended states along with the localized states. Based on Anderson’s theory [11], Mott [12] argued that the spatial fluctuations in the potential caused by the configurational disorder in amorphous materials may lead to the formation of localized states which do not occupy all the different energies in the band. A band gap may however exist in amorphous semiconductor due to short range order in them. Due to 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 this tailing was expected to be enhanced in alloys which contain compositional disorder in addition to positional disorder. Mott postulated furthermore that there should be a sharp boundary between the energy ranges of extended and localized states. The states were localized in the sense that an electron placed in a region would not diffuse at zero temperature to other regions with corresponding potential fluctuations; the conduction in localized states takes place by hopping process with the help of thermal energy. The mobility of charge carriers therefore changes suddenly from a finite value to zero in the band tails.

Several models are discussed below to describe the properties of amorphous materials

1.4.1 Cohen-Fritzsche-Ovshinsky (CFO) Model:

In CFO model [13] the tail states extend across the gap. Fig. 1.3 shows the CFO model in which mobility gap $E_c - E_v$ contains only localized states. This gradual decrease of the localized states destroys the sharpness of the conduction and valence band edges. The authors suggested that in the chalcogenide glasses, the disorder was so great that the tails of the conduction and valence bands
overlap, leading to an appreciable density of states in the middle of the gap. Due to overlapping of the bands, there were states in the valence band, ordinarily filled, that have higher energies than states in the conduction band that were ordinarily unfilled. A redistribution of the electrons must take place, forming filled states in the conduction band tail, which were negatively charged and empty states in the valence band, which were positively charged. This model, therefore, ensures self-compensation and pins the Fermi level close to the middle of the gap. Later, a similar model was proposed by Spear [14] to calculate barrier formation and photoconductivity in amorphous silicon. One of the major objections against the CFO model was the high transparency in IR region of the amorphous chalcogenides below a well-defined absorption edge.

1.4.2 Davis-Mott Model:

Davis and Mott [15] proposed this model according to which the tails of localized states should be rather narrow and should extend a few tenths of an electron volt into the forbidden gap. Fig. 1.4 shows the Davis-Mott model; here, $E_c$ and $E_v$ represent the energies which separate the ranges where the states were localized and extended. In this model the authors proposed the existence of a band of compensated levels near the middle of the gap, originating from defects in the random network, in order to pin the Fermi level. The center band has been splitted into a donor and an acceptor band, which will also pin the Fermi level. This model suggests that hopping conduction can take place in the localized states near the Fermi level.

1.4.3 Mott, Davis and Street (MDS) Model

Mott-Davis and Street (MDS) proposed a band model in 1975 to explain the behaviour of amorphous semiconductors [16, 17]. The mobility edges for electrons and holes are at $E_c$ and $E_v$. The localized states originate due to lack of
long-range order while the defect states are due to various kinds of defects in the structure. The center band splits into two levels forming donor and acceptor bands as shown in Fig. 1.5. They considered the states near Fermi level due to defects, particularly, dangling bonds. Their model is based on Anderson's idea [18] that paired electron states are preferred in chalcogenide glasses \( i.e., \) \( D_j \) and \( D^+ \). In some structural configurations, the atoms are not able to share the electrons and the bond breaks. Hence, a dangling bond emerges out of this unstable situation. If a dangling bond is singly occupied, it is neutral (\( D^\pm \)) indicating that an Electron Spin Resonance (ESR) signal is expected. In some cases, a dangling bond can attract an additional electron and, thus providing a lone pair, it is designated as \( D_j \), indicating that there will be no ESR signal, and \( D^+ \), when the bond loses even the single electron it has, giving rise to a hole representing a bond without any spin. This model predicts no ESR, Para-magnetism and can explain many other properties of chalcogenide glasses.

1.5 Chalcogenide Glasses:

Chalcogenides are materials containing at least one of the chalcogens, S, Se or Te usually in combination with more electropositive elements such as As or Ge. Many elements can combine with these chalcogens to form stable amorphous and crystalline chalcogenide phases exhibiting a variety of unique optical and electrical properties. Comparison of chalcogenide glass with other materials is shown in Fig. 1.6. Chalcogenide glasses, for example, are amorphous semiconductors with band-gaps typically~ between 0.6 and 1.4eV. Since their discovery in the 1950's chalcogenide glasses have been studied in great detail in hopes of exploiting several unusual properties unique to amorphous semiconductors.
Figure 1.3: Cohen, Fritzche and Ovshinsky Model (CFO).

Figure 1.4: Davis and Mott Model.

Figure 1.5: Mott, Davis and Street Model.
The 2-fold coordination of chalcogenides results in a very flexible network which can easily incorporate dopant electrons into low energy bonds.

![Diagram of material comparison](image)

**Figure 1.6: Comparison of chalcogenide glass with other materials.**

The most widely exploited property of chalcogenide glasses is their large infrared transmittance in combination with their chemical and mechanical durability. In comparison to other IR optical materials such as fluorozirconate glasses which transmit only up to 7 micron, chalcogenide glasses can transmit well beyond 10 microns, and although chloride, bromide and iodide glasses transmit to longer wavelengths than chalcogenides, the chemical and mechanical durability of chalcogenide glasses has resulted in their widespread use in IR-optics and specialized fiber optic applications.

The most unique property of chalcogenides, however, is their ability to reversibly switch from a resistive to a highly conductive state. Large reversible changes in optical characteristics are also possible. Pioneering work in this area has led to the development of chalcogenide-based memory devices such as "Phase-Change Erasable" (PCE) optical disks. Although chalcogenide
glasses are semi-conducting in the amorphous phase, they can become highly conductive in the crystalline phase, hence their electrical switching ability.

The unique bulk properties of chalcogenides become even more interesting when they are in thin film form. Thin films can be formed in several ways. Thermal evaporation and subsequent vapor deposition of bulk chalcogenide melts onto a substrate is the simplest method of preparing thin films, however different elemental evaporation rates can result in unexpected film stoichiometry. Sputtering is another method that can produce superior films with very well characterized stoichiometries at the cost of a more complex technique. Wet chemistry and pulsed laser vapor deposition have also been employed, however thermal evaporation and vapor deposition is the most widely used technique.

1.6 Defect States in Chalcogenide Glasses:

The conductivity in chalcogenide glasses is not much affected by doping. It has been confirmed by various investigations that 8-N rule given by Mott is applicable for chalcogenide glasses, particularly for Ge$_{1-x}$Se$_x$ system to explain the effect of doping. According to 8-N rule all the available electrons of the impurity made covalent bonds with the surrounding atoms.

Experimental results indicate that Fermi level was pinned and doping have been quite difficult in chalcogenide glasses. This was understood if one assumed a considerable density of defect states (DOS) in the mobility gap of these materials. However, unlike other amorphous semiconductors, electron spin resonance was not observed in these glasses. The variable range hopping due to localized states near Fermi level as suggested by Mott was also not observed in chalcogenide glasses under normal conditions of preparation. These materials show diamagnetic behaviour unlike tetrahedral amorphous semiconductors which show paramagnetic behaviour.
In chalcogenide glasses, non crystalline structure is indicated by the absence of Electron Spin Resonance (ESR) [19], curie Para-magnetism at low temperature [20] and Variable Range Hopping (VRH) [21]. Chalcogenide glasses contain high concentration of defect states known as "broken bond" or "dangling bond". Photoluminescence study [22], photoconductivity [23], drift mobility [24] and that of pinned Fermi level confirms the existence of dangling bond.

Absence of ESR signal and Para-magnetism of curie type at low temperatures shows the absence of unpaired electrons, which is a characteristic feature of the broken bond. To explain this, Street and Mott [17] said that to transfer an electron from one such site to another would be an exothermic process. The energy (Hubbard U) lost by putting another electron into singly occupied lone-pair orbital to form a D (negative dangling bond) was more than compensated by the energy gained when the D centre formed a bond between its empty lone-pair orbital and the fully occupied lone-pair on a neighbour (the neighbour being then triply coordinated as pointed out by Kastner et al.). The bond formed is called dative because both electrons come from the same orbital. These centers would then pin the Fermi energy but give no spin signal. The term negative Hubbard U denotes the hypothesis that the energy to take an electron from one dangling-bond state and put it in another is negative and this can only occur through a distortion of the D centre. The spin pairing can be described by the following reaction

$$2D^0 \rightarrow D^+ + D^- \quad \text{(1.1)}$$

It is assumed that above reaction is exothermic due to electron-phonon interaction. For the reaction to be exothermic, following condition should hold

$$W_1 + W_2 - B < 0 \quad \text{(1.2)}$$
where $B$ is the optical band gap, $W_1$ is the energy (distortion plus electronic) required to take an electron from the valence band and place it on a $D^0$ centre, thereby turning it into $D^-$, and $W_2$ is the total energy necessary to take an electron from a $D^0$ centre and place it in the conduction band. The thermal energy required to take two electrons out of a $D^-$ centre and to place them in the conduction band is given by

$$W = B - W_1 + W_2$$

where $W_M$ is the maximum energy required to remove two electrons from a $D^-$ centre i.e. when infinitely separated from a $D^+$ centre. Schematic illustration of thermal energy levels has been shown in Fig. 1.7. $W_M$ can also be understood as being simply twice the energy between the Fermi level and the conduction band; the Fermi energy is the average energy per electron to take an electron out of the highest-lying occupied state ($D^-$) and place it in the lowest-lying unoccupied state (at the conduction band edge). Chalcogenide materials are in general p-type, exhibiting simply activated dc conductivity of activation energy $\Delta E$. Thus, $W_M$ can be written equivalently as

$$W_M = 2 (B - \Delta E)$$

Since the Fermi level for these materials often lies near mid gap, so $\Delta E \approx \frac{1}{2} B$, a consequence of the fact that $W_1 \approx W_2$, which indicates that to a first approximation we may take $W_M \approx B$. 


Figure 1.7: Schematic illustration of thermal energy levels associated with electronic transitions between $D^+$, $D^-$ and $D^0$ centers.

1.7 Preparation Techniques of Chalcogenide Glasses:
1.7.1 Quenching Technique:

In this technique, materials are prepared in glassy form by rapid cooling of the melt. For the preparation of glasses the required compositions are prepared by weighing the constituent elements in desired atomic percentages and then sealed in quartz ampoules with a high vacuum $\sim 10^{-5}$ Torr. Sealed ampoules are kept in a furnace at a temperature for components to melt. The ampoules are frequently rocked for about ten hours to make the melt homogeneous. The quenching is done by dropping the quartz ampoules suddenly in ice cooled water or liquid nitrogen, depending upon the requirement. In some cases, air quenching is sufficient, where air is blown on the heated ampoules by an air blower.
1.7.2 Thermal Evaporation Technique:

In this technique, the materials are made amorphous in the form of thin films by creating high vacuum in the Bell Jar and heating the filament containing the material, by passing electric current in it. The substrate used may be glass or any other suitable material. Substrate temperature could also be varied by mounting a heater inside the bell jar. The essential feature of this technique was that atomic surface mobility was greatly diminished because of the cold substrate, causing the adatoms to be 'frozen' in the random positions at which they arrive.

1.7.3 Flash Evaporation Technique:

The major problem with the thermal evaporation technique was 'differential evaporation' due to which variability in purity and compositions of the thin films occur. This problem has been overcome to a great extent by flash evaporation technique. This technique is similar to thermal evaporation except that powdered material is dropped steadily on already heated filament. In addition to the coating unit, an AC magnetic field is established to produce vibrations in a magnetic strip containing material.

1.7.4 Sputtering Technique:

More complicated but more flexible than thermal evaporation technique, it consists of the bombardment of a target by energetic ions from low pressure plasma, causing erosion of materials, either atom by atom or as clusters of atoms and subsequently depositing of film on the substrates. The simplest way to induce sputtering was to apply a high negative voltage to the target surface, thereby attracting positive ions from the plasma. However, the d.c. sputtering process was feasible only when target is sufficiently conducting so that target could act as electrode.
1.7.5 Pulsed Laser Deposition (PLD) Technique:

In case of chalcogenide-based materials, application of classical thin films deposition techniques (vacuum thermal evaporation, sputtering etc.) leads often, due to different volatility of components of starting material, to non-homogeneous thin films. The PLD technique is a promising method for preparation of thin films with stoichiometry close to used targets of complex composition. In this technique, radiations from gas-based excimer laser systems or solid state lasers e.g., YAG:Nd$^{3+}$ laser was made to fall on solid-state materials, resulting in evaporation, excitation and plasma formation. The chemical bonds on the surface of target material gets broken by high energy photons, material was atomized and evaporated independently on volatility of its fragments. The evaporated particles form a plume that contains energetic species such as atoms, molecules as well as electrons and ions. The formed vapours and plume particles were subsequently deposited on appropriate substrate.

1.7.6 Glow Discharge Deposition Technique:

In this technique there is production of plasma in a low pressure gas by the chemical decomposition of the gas itself, leading the deposition of a solid film on a substrate kept in plasma. The plasma is produced by the application of an r.f. field, either using inductive coupling or capacitive coupling.

1.7.7 Chemical Vapour Deposition Technique:

It is analogous to the glow discharge method in that both depend on the decomposition of a vapour species. This method relies on the thermal energy for the decomposition and the r.f. field is applied to heat up the substrate upon which the vapour decomposes.
### 1.8 Applications of Chalcogenide Glasses:

Four kinds of applications of chalcogenide glasses are commercially available or practically utilized. These rely upon the unique features of chalcogenide glasses: quasistability, photoconductive properties, infrared transparency, and ionic conduction.

The first is the phase-change phenomenon used in erasable high-density optical memories [25]. The product utilizes semiconductor lasers and chalcogenide films such as GeSbTe with a thickness of ~15 nm. The reflectivity change between amorphous and crystalline phases is monitored with a weak light beam. The present memory capacity is about 5 GB/disk, which is still increasing [26].

The second category is photoconductive applications such as photoreceptors in copying machines and X-ray imaging plates [27, 28, 25]. In a photoconductive target in videocons, avalanche multiplication in amorphous selenium films is employed, which substantially enhances the light sensitivity so that star images can be taken.

The third application is purely optical [27-29]. That is, since the chalcogenide glasses (CGs) are transparent in IR regions, it can be utilized for IR optical components such as lenses and windows. Application of CGs in optics includes energy management, thermal fault detection temperature monitoring and night vision [30]. Black body radiation emitted by room temperature objects such as human body is in the 8-12 µm regions, where Se-Te based glasses are applicable for thermal imaging. It can also be utilized for IR-transmitting optical fibers. Fibers have also been employed as a matrix incorporating rare-earth ions, such as Er$^{3+}$. Such rare-earth ion doped chalcogenide glasses are promising for preparing functional fibers such as optical amplifiers. Compact fibre-optic systems based on CG fibres have been found suitable for low power transmission, which has applications for
industrial welding and also for microsurgery in medical and biological conditions [31, 32]. Infrared CG fibres have been found useful for biosensing experiments on liver metabolism, tumor detection, serum analysis and IR fingerprints of human lung cells in different metabolic conditions.

Lastly, chalcogenide glasses containing group I elements such as silver are used as high-sensitivity ionic sensors [27, 28]. Some lithium containing glasses can also be utilized as solid-state electrolytes in all-solid batteries.

1.9 Selection of the Materials:

1.9.1 Selenium Germanium System:

Ge-Se glassy system is an interesting system as it is a combination of two different kinds of amorphous semiconductors: a-Ge, which contains unpaired electrons; and a-Se, where defects are charged and unpaired electrons are not present, as evident from electron spin resonance and magnetic susceptibility measurements.

This difference arises from the dissimilarity in the short-range structures of these two systems. a-Ge has tetrahedral structure which is more rigid than the flexible structure of a-Se, which has chain structure in two fold coordination. The addition of another element in binary systems has been quite useful in improving some of the properties of glassy semiconductors. Though the addition of the third element stabilizes the structure, which makes the ternary system more stable thermally, the density of defect states is changed, which in turn affects its properties [33-35]. These glasses have a threshold in their electronic [36], thermal [37], vibrational [38] and structural [39] properties when average coordination number ($<r>$) approaches 2.4.

There is strong evidence of the existence of broken chemical order and structural heterogeneity in Ge containing chalcogenide glasses. Studies of binary GeSe$_2$ chalcogenide by Raman spectroscopy, suggests a
chemically ordered structural network. Raman measurements of GeSe$_2$ glasses in bulk form performed at a high spectral resolution and combined with Mossbauer spectroscopy using Ge replacing Sn as a probe atom, demonstrated broken chemical order and microscopic phase separation [40]. Studies of Ge$_x$Se$_{1-x}$ bulk glasses of near stoichiometric GeSe$_2$ compositions by x-ray and neutron diffraction provide more evidence for the legitimacy of the cluster model [41-44]. Yet investigations of the local coordination environment of Ge atom in the Ge-Se glasses in both bulk and film forms using extended x-ray absorption fine structure (EXAFS) spectroscopy yielded results supporting a high degree of homogeneity and chemical order in the structure of these glasses [45, 46]. In case of a-Ge-Se binary glass, two types of structural arrangements could be revealed from Raman spectra [47]. One arrangement consists of mostly the fragments built with corner-sharing and edge-sharing tetrahedral Ge(Se$_{1/2}$)$_4$, which form the structure. Another structural organization contains a larger amount of ethane-like Ge$_2$(Se$_{1/2}$)$_6$ units forming chemically different chain clusters in the structure [40]. It also exhibits a higher ratio of corner-sharing to edge-sharing tetrahedral Ge$_2$(Se$_{1/2}$)$_4$ units. Variation of the Ge fraction in the vicinity of stoichiometric GeSe$_2$ composition has a significant effect [41-44]. If the Ge fraction is below 30 at. %, the amount of fragments, built with Ge$_2$(Se$_{1/2}$)$_6$ units, is small. With an increase of Ge fraction to 33 at. %, Ge$_2$(Se$_{1/2}$)$_6$ relative concentration starts to grow and rises rapidly when the Ge fraction reaches 36-38 at. %. The structural changes are accompanied by variation in measured optical properties. The formation of Ge$_2$(Se$_{1/2}$)$_6$ chain clusters lead to a noticeable increase in the refractive index and the absorption edge wavelength, which appear to have distinct values for the structures with high and low Ge$_2$(Se$_{1/2}$)$_6$ relative concentrations, due to abrupt
threshold-like growth behaviour of Ge$_2$(Se$_{1/2}$)$_6$ chain clusters. In binary glasses, the structural changes manifest primarily in altering the relative concentration of Ge$_2$(Se$_{1/2}$)$_3$ chain clusters and Se clusters and very slight variation of the ratio between edge-sharing and corner-sharing Ge$_2$(Se$_{1/2}$)$_4$ tetrahedra in Ge-Se clusters, and are promoted mostly by slight changes in glass composition.

The effect of incorporation of third element in binary chalcogenide glassy alloys has always been an interesting problem in getting relatively stable glassy alloys as well as to change the conduction from p to n as most of these glasses show p type conduction only. Ge-Se system exhibits properties, which are unusual, and possibly unique, relative to other semiconductors. These unusual characters have obviously added much flavour to the stimulated study. Amorphous semiconductors from Se-based system such as Ge$_x$Se$_{1-x}$ have attracted much attention in recent years. Ge$_x$Se$_{100-x}$ is being actively investigated as high efficiency semiconductors for xerography, switching and memory devices and reversible phase change optical recording [48-49]. Exposure to light or heat that excites electron hole pairs produces structural changes in nearly all chalcogenide glasses. The results change with atomic configuration and a subsequent change in physical properties such as structure, optical and electrical properties of material [50-51]. The coordination number of Ge is 4 and Se is 2, so at $x = 20$, the value of $< r > = 2.4$ in a-Ge$_x$Se$_{100-x}$ system. What happens to the Ge$_{20}$Se$_{80}$ system, when it is alloyed with a second element of group IV, is very important from the basic as well as application point of view.

In Ge-Se and Se-In systems, some metallic additives have been found [52-58] to change conduction from p type to n type and hence these binary systems are of great importance. It was known that Ge$_x$Se$_{1-x}$ was one of the best
glass former in the chalcogenide family and forms glasses for $x < 43\%$ [59]. Chalcogenide glasses in Ge-Se system were interesting materials for infrared optics having a large range of transparency and good mechanical properties such as hardness, adhesion, low internal stress and water resistance. Therefore Ge-Se alloys were good candidates as arsenic-free IR transparent materials.

### 1.9.2 Selenium Tellurium System:

Among chalcogenide glasses, Se-Te binary system have gained much importance because of their higher photosensitivity, greater hardness, higher crystallization temperature and smaller aging effects as compared to pure Se glass; these advantages made these alloys preferred in xerography. This system is very important for the better understanding of the transport mechanism in chalcogenide glasses because it has been demonstrated that the addition of Te to Se progressively decreases both electron and hole drift mobility and increases the integrated number of deep traps and broadens the distribution of both deep and shallow electronic gap states. Tellurium alloys have often used for the active layer of memory devices because they have low melting points. Se-Te based alloy films were thought to be one of the most promising media which make use of a phase change between an amorphous state and a crystalline state. Structure of the amorphous Se-Te system, prepared by quenching from the melt, have been regarded as a mixture of eight-membered rings, $\text{Se}_6\text{Te}_2$ mixed rings and Se-Te chains. Strong covalent bonds exist between the atoms in the rings and the chains. It have already been reported that the addition of a strong electropositive element may leads to a cross-linking between the chains, promoting in this way the formation of a three dimensional network.

Literature survey on the effect of third element as an additive to the binary chalcogenide alloys reveals that it brings structural stability to the binary
systems although the increase in the density of defect states is quite likely in multicomponent alloys as compared to binary ones. As many electrical properties in these glasses depend on the density of such defect states, an independent measurement of these states was required for a better understanding of these materials and possible improvement in them. The candidate has chosen here the Se-Ge and Se-Te binary system in order to see the effect of third element as an impurity on the density of defect states by measuring the transport properties of these binary and ternary chalcogenide glassy alloys.

1.10 Review of Electrical and Photo-Electrical Properties in Chalcogenide Glasses and Selection of the Problem:

The emergence in recent years of amorphous semiconductors with potential theoretical and practical applications has given a great stimulus to studies of basic properties of these materials. The field of disordered materials, in general and amorphous semiconductors, in particular is very exciting because it is relatively new and offers many challenges to scientists both experimentalists and theoreticians. The development of electronic devices proceeded slowly because of the lack of adequate knowledge of basic physics of these materials. Though overall progress in glass science has been considerable over the last two decades and various models has been suggested to explain many facets of amorphous semiconductors, but the physicists feel that much remains to be explored. Amorphous semiconductors are non crystalline materials. They lack long range periodic ordering of their constituent atoms but rather they contain covalently bonded atoms arranged in an open network with ordering up to third or fourth nearest neighbours.

Recent advances in our understanding of the electronic structure of amorphous semiconductors have followed from the postulate that well defined
defects were present in these materials and in fact, since some of these defects have a low creation energy, they could be present in concentrations sufficiently large to control the transport behaviour of these materials. The existences of defects in crystalline solids were well known and of great importance, but the constraints of long range periodicity limit their nature.

The role of defects in amorphous semiconductors is now appreciated as being just as important as in their crystalline counterparts. Experimentally improved deposition techniques have produced materials in which the properties of defects were now clearly distinguishable from those of the general disorder. Since the density of these defect states (DOS) is a key parameter of amorphous substances, the vast utilization of semiconductors in modern electronics demands an extensive study on the nature of these defects present in these semiconducting materials. However, the replacement of crystalline semiconductors with amorphous ones has been limited due to the presence of high density of inherent defect states in amorphous semiconductors.

Among the many amorphous semiconductors, hydrogenated amorphous silicon (a-Si:H) prepared by the glow-discharge method was one of the most widely used material. It was one of the amorphous material which, when prepared under suitable preparation conditions could be efficiently doped due to a low density of states in the band gap and hence new electronic devices could be constructed. Chalcogenide glasses were another type of amorphous material which has recently drawn great attention due to their potential use in various solid state devices. Chalcogenide glasses are rather insensitive to the addition of impurities. The electrical conduction in these glasses is still hard to control by impurities, it remains almost intrinsic in these glassy
semiconductors. This is due to the fact that the Fermi level in these materials is pinned near the middle of the band gap by valence alternation pairs.

Due to their various properties chalcogenide glasses are very attractive candidates for different technological applications. The common feature of these glasses is the presence of localized states in the mobility gap due to absence of long range order as well as various inherent defect states. Since the concentration of intrinsic defects were very high in case of chalcogenide glasses, a large amount of impurity atoms were needed to exceed the intrinsic defect states. Mostly, the high impurity concentration brings the material out of glass forming region. However, there have been reports that glasses of the Se-Ge, Se-In, Ge-Se-Te, Ge-Te systems exhibit the phenomenon of carrier-type reversal (CTR) or p to n transition when doped with high concentrations of certain heavy elemental metallic impurities like Bi or Pb. The exact reason for the appearance of n-type conduction is still not very clear but it have been explained by some authors that when these metallic impurities were added, the number of holes decreases in these systems, while the number of electrons increases. These two effects together shift the Fermi level towards the conduction band resulting in p to n transition at a particular impurity concentration. Nevertheless, beyond any doubt, the above reports have provided a break through that doping could be achieved in these glassy semiconductors. The effect of impurity in chalcogenide glasses depends upon the composition of the glass, the chemical nature of the impurity, the method of doping and the value of impurity concentration and therefore, it is of interest to study various physical properties of these glasses as a function of composition and impurity.

Based on some physical properties the covalently bonded non-crystalline semiconductors have been divided [60] into two main categories: (i)
Ge type, which shows ESR signal, paramagnetic behaviour and variable range hopping conduction and (ii) Se type, which does not show the above properties under normal conditions due to the presence of paired defect states. The Ge\textsubscript{x}Se\textsubscript{1-x} system may belong to either of the categories depending upon the value of x. Due to this peculiarity, various physical properties such as photoluminescence [61,62], drift mobilities [63], photocontraction [64] and photoconductivity [65] have been studied in detail and it have been established that the properties were highly composition dependent.

Asha Bhat et al. [66] have studied compositional dependence of photoluminescence in Ge\textsubscript{20}Se\textsubscript{80-x}Bi\textsubscript{x} and Ge\textsubscript{20}Se\textsubscript{70-x}Bi\textsubscript{x}Te\textsubscript{10}. They have observed that addition of Bi brings out reduction in the relative concentration of D\textsuperscript{+} as compared to D\textsuperscript{-} defects. The imbalance accompanied by the contribution of extra electrons brings out n-type conduction in Bi doped glasses.

Kaluzny et al. [67] have measured temperature dependencies of direct electrical conductivity, temperature and frequency dependencies of complex permittivity and complex electrical modulus in Ge\textsubscript{0.2}Se\textsubscript{0.8-x}Te\textsubscript{x} glasses pure and doped by Pr\textsuperscript{3+} and Er\textsuperscript{3+}. They found that these glasses exhibit only one mechanism of electrical conductivity with activation energy U = (0.95 ± 0.10) eV. They showed that measured glasses are single-phase but not homogeneous, with high concentration of the point defects due to the presence of Te and they are stable up to the temperature of 180°C.

Ganesan et al. [68] have studied the composition dependence of the thermal diffusivity of Pb\textsubscript{x}Ge\textsubscript{42-x}Se\textsubscript{58} and Pb\textsubscript{20}Ge\textsubscript{y}Se\textsubscript{80-y} by the photoacoustic technique. The measurements show an unusual behaviour at p to n conduction changes. In Pb\textsubscript{x}Ge\textsubscript{42-x}Se\textsubscript{58} glasses, the change is more
prominent than in the \( \text{Pb}_{20}\text{Ge}_{y}\text{Se}_{80-y} \) glasses. The thermal diffusivity value shows minima at the p to n transition threshold and then increase with corresponding increases of Pb and Ge concentration in the glasses. The addition of Pb disturbs the equilibrium between Se and Se-centers, thus unlocking the Fermi level.

Mehta and group [69] performed differential scanning calorimetry (DSC) at different heating rates under non isothermal conditions to study the crystallization kinetics of \( \text{Se}_{68}\text{Ge}_{22}\text{Pb}_{10} \) chalcogenide glasses. They determined different kinetic parameters such as energy of crystallization, the order parameter, the rate constant and its frequency factor. They found that \( E_c \) values obtained by four different methods are in good agreement with each other. By finding the values of Avrami’s index, they concluded that in glassy \( \text{Se}_{68}\text{Ge}_{22}\text{Pb}_{10} \) two crystallization (two & three dimensional group) mechanisms are working simultaneously during its amorphous to crystalline transformation. They found that rate constant increases with increase in temperature as well as with increase in heating rate.

Chandel and coworkers [70] studied frequency and temperature dependence of ac conductivity on \( (\text{Ge}_{20}\text{Se}_{80})_{0.90}\text{Sn}_{0.10} \) glassy alloy in the frequency range of 2-50 kHz and in the temperature range of 273-373 K. Dielectric constant \( (\varepsilon') \), dielectric loss \( (\varepsilon'') \) and loss angle \( (\tan\delta) \) were calculated. Temperature dependence of dielectric loss showed relaxation peaks as a function of temperature and these peaks shifted towards the higher temperature as the frequency was increased. Results were explained in terms of dipolar relaxation with a distribution of relaxation times.

P. Petkov [71] studied the kinetics of the processes of the evaporation and condensation of thin films of the glassy system GeSeY, where \( Y = \text{Ga, Tl, B} \). Some basic electrical characteristics of the investigated semiconductor film were calculated applying the Christov theory for injected current electrons.
Sharma et al. [72] have calculated the indirect and direct energy gaps of the Ge$_{20}$Se$_{80-x}$Bi$_x$ thin films (x=0, 4, 6, 8, 10, 12). They have found that both direct and indirect band gaps decrease with increasing the bismuth content. The indirect band gap decreased from 1.48 eV to 1.16 eV and the direct band gap decreases from 2.14 eV to 1.68 eV when Bi content is increased from x = 0 to x = 12.

Mitkova et al. [73] have shown that ternary (Ge$_x$Se$_{1-x}$)$_{1-y}$Ag$_y$ bulk glasses in the Se-rich region (x < 1/3) are intrinsically phase separated into an Ag$_2$Se-rich glass and a residual Ge$_{1-t}$Se$_{t}$ backbone (t > x at y ≠ 0) with Ag acting as a network modifier. Whereas Ge-rich glasses (x ≥ 2/5) are homogeneous, wherein Ag acts as network former, replacing available Ge sites of the backbone to be 3-fold coordinated to Se.

Takehi et al. [74] have studied optical, electrical and structural properties of amorphous (Ge$_{0.3}$S$_{0.7}$)$_{100-x}$Ag$_x$ and (Ge$_{0.3}$Se$_{0.7}$)$_{100-y}$Ag$_y$ films over the composition (0 ≤ x ≤ 67, 0 ≤ y ≤ 40). They have found that dc resistivity decrease drastically but the optical band gap decreases gradually with an increase in Ag content. The structure of the S- and Se-based films depends significantly on the Ag content and their compositional trends resemble each other. Phase separation into Ag-poor and Ag-rich phases occurs in the Ag-rich films of both the systems (x > 45, y > 22).

I-V Characteristics at various fixed temperatures in amorphous thin films of Ge$_{22}$Se$_{78-x}$Bi$_x$ and Ge$_x$Se$_{80-x}$Te$_{20}$ where 0≤x≤10 were studied by S. K. Dwivedi and group [75]. They demonstrated that at high fields, results for Bi could be interpreted in terms of SCLC for a uniform distribution of traps however in case of a-Ge$_x$Se$_{80-x}$Te$_{20}$ system mechanism of conduction was Poole Frenkel type.

Thakur et. al. [76] carried out photoelectrical measurements in thin films of (Ge$_{20}$Se$_{80}$)$_{0.98}$Sn$_{0.02}$ glassy alloy as a function of temperature and intensity.
Their results showed that conduction in glassy alloy is an activated process having single activation energy in the temperature range (289K-333K) and intensity dependence of photoconductivity ($\sigma_{ph}$) follows a power law with intensity $F$, $\sigma_{ph} \propto F^\gamma$, where value of $\gamma$ was found to be 0.5.

Ahmed et. al. [77] carried out dc conductivity measurements on the bulk amorphous $\text{Ge}_{14}\text{Se}_{86-x}\text{Tl}_x$ samples where $x = 22, 23.5, 25, 28$ mole % and temperature range 240 K - 420 K. D.C. conductivity was found to increase with increasing content of Thallium and measuring temperature.

The temperature dependence of electrical conductivity measurements in dark and in presence of light in vacuum evaporated thin films of a-$(\text{Ge}_{20}\text{Se}_{80})_{99.5}\text{Cu}_{0.5}$ were studied by Thakur and group [23]. It was found that dark conductivity increases exponentially with temperature and photoconductivity is also thermally activated. Their measurements ensured the presence of mono and bimolecular recombination region. Transient photoconductivity measurements at different temperatures and light intensities showed that the photocurrent passes through a maxima before attaining the steady state.

Singh et. al. [78] studied the effect of Bi impurity on the ac conductivity of a-$\text{Ge}_{20}\text{Se}_{80}$ glasses. Frequency dependent ac conductivity measurements showed that the value of conductivity slightly decreases at low concentration (4 at. %) and increases drastically at higher concentration of Bi. It was also found that the addition of Bi brings out a reduction in the relative concentrations of $D^+$ as compared to $D^-$ defects.

Transient Photoconductivity measurements were made in vacuum evaporated thin films of $\text{Se}_{0.80-x}\text{Ge}_{0.20}\text{Ag}_x$ at different intensities, temperatures and illumination times by Sharma and coworkers [79]. It was shown that the persistent photoconductivity increases with an increase in intensity and illumination time while the quantity decreases with increase in temperature.
The persistent photoconductivity effect was found to be suppressed on increase of Ag concentration in a- Se$_{0.80-x}$Ge$_{0.20}$Ag$_x$, which was explained in terms of smaller effect of light induced defects due to higher concentration of inherent structural defects in dark at higher concentration of Ag.

Among chalcogenide glasses Se-Te glassy alloy also have gained much importance because of their superiority over amorphous selenium. The structure of a-Se [80, 81] and the effect of alloying Te into a-Se [82, 83] have been studied by various workers. Their results have shown that a-Se contains long polymeric chains and eight members rings in various proportions as its structural units, which were dissociated by the addition of Te in a-Se. This makes Se-Te alloys more important due to their attractive advantages such as higher photosensitivity, greater hardness, higher crystallization temperature and lesser aging effects as compared to pure a-Se. Due to these advantages, Se-Te alloys could be used as recording layer materials in optical phase change (PC) technique [84]. Addition of Se into a Te alloy improves the corrosion resistance. Therefore, Se-Te based alloy films were thought to be one of the most promising media which make use of a phase change between an amorphous state and a crystalline state.

Mehta et. al. [85] studied the temperature and frequency dependence of a.c. conduction in in glassy Se$_{100-x}$Te$_x$ (x = 10, 20 and 30) over different range of temperatures and frequencies. the a.c. conductivity behaviour of selenium–tellurium system (Se$_{100-x}$Te$_x$) was explained and density of defect states was determined by correlated barrier hopping (CBH) model. It was shown in the results that bi-polaron hopping dominates over single-polaron hopping in this glassy system and the values of density of charged defect states increase with increase in Te concentration.

Dielectric properties of glassy system Se$_x$Te$_{79-x}$Ge$_{21}$, with x = 11, 14, 17 at.%., were studied by F. Salman [86] at temperatures 300 to 450 K and over a
wide range of frequencies (50 Hz to 500 kHz). Experimental results indicated that the ac conductivity and the dielectric constants depend on temperature, frequency and Se content. The mechanism of ac conductivity was interpreted in terms of the correlated barrier hopping model (CBH). The activation energies were estimated and discussed. The dependence of ac conductivity and dielectric constants on the Se content $x$ was also interpreted as the effect of Se fraction on the positional disorder.

Temperature and intensity dependence of photoconductivity ($\sigma_{ph}$) and temperature dependence of dark conductivity ($\sigma_d$) was studied in a- Se$_{85}$Te$_{15}$ and a- Se$_{83}$Te$_{15}$Sn$_2$ thin films by Sharma and group [87]. The results showed that dark conductivity increased while activation energy and photosensitivity decreased with the addition of Sn. The results were explained on the basis of the increase in the density of states on Sn incorporation in the Se$_{85}$Te$_{15}$ binary alloy.

Mehta and group [88] reported the Differential Scanning Calorimetric (DSC) study of some Ag doped Se - Te chalcogenide glasses. Activation energy of crystallization ($E_c$) was evaluated which was found to be decreased due to addition of Ag in binary alloy Se$_{70}$Te$_{30}$. The compositional dependence of ($E_c$) in ternary alloys showed a reversal in the trend at 4 at. % of Ag.

Soltan and coworkers [89] studied the effect of composition and annealing on optical properties and electrical conduction of Se$_{85-x}$Te$_{15}$Sb$_x$ glasses. They found a decrease in the activation energy with the addition of Sb and an increase in the electrical conductivity with an increase in the annealing temperature.

Transient photoconductivity experiments in amorphous thin films of Se$_{75}$Te$_{20}$Ag$_5$ were carried out by Sharma and group [90]. They found an anomalous behaviour of rise and decay. Under illumination photoconductivity first increased, attained a maximum and then decreased. When light is turned
off, photoconductivity decayed very fast, became negative and then leveled off very slowly.

Majeed Khan et al. [91] studied the I-V characteristics of thin films of a-Se$_{80}$Te$_{20-x}$Pb$_x$ (where x = 0, 2, 6 and 10) at high field and demonstrated that current could be fitted to the theory of space charge limited conduction in case of uniform distribution of localized states in the mobility gap of these materials. They found an increase in DOS by the addition of Pb in binary Se-Te glassy system.

Singh et al. [92] carried out dc conductivity measurements at high electric fields in vacuum evaporated thin films of the Se$_{80-x}$Te$_{20}$Ag$_x$, (where x = 0, 5, 10 and 15). At high fields non ohmic behaviour was observed and they confirmed the presence of SCLC in all the samples. DOS near Fermi level was calculated which did not change significantly with increasing concentration of Ag in pure binary Se$_{80}$Te$_{20}$ glassy system.

Sharma and group [93] carried out the transient photoconductivity measurements on a-Se$_{85-x}$Te$_{15}$In$_x$ (where x = 0, 4 and 10) thin films. The results showed an increase in the density of localized states in the mobility gap of SeTe binary alloy on addition of In. Both $\sigma_d$ and $\sigma_{ph}$ increased after the addition of In. A decrease in $\Delta E_d$ and $\sigma_{ph}/\sigma_d$ was found on increasing the concentration of In.

Singh et al. [94] have carried out a systematic study of I-V parameters on a-Se$_{80-x}$Te$_{20}$Cd$_x$ thin films both at high fields and low fields at various fixed temperatures. They found SCLC at high fields. DOS near Fermi level was calculated, which did not change significantly with the incorporation of Cd in pure binary Se$_{80}$Te$_{20}$ glassy system.

Tripathi et. al. [95] studied the effect of Sb additive on the dark conductivity and photoconductivity in a-Se$_{85}$Te$_{15}$ binary alloy. They found an increase in $\sigma_d$, $\sigma_{ph}$ and decrease in the value of activation energy after the
addition of Sb. These results indicated the increase in DOS with the increase in Sb concentration.

Saraswat et. al. [96] carried out I-V characteristics measurements on Se\(_{85-x}\)Te\(_{15}\)Sb\(_x\) glassy thin films. They found that the film containing 4 at. % of Sb allows the maximum current to pass through itself as compared to other counterparts of the series which was explained on the basis of bond formation between Se and Sb at different compositions. Conduction mechanism was found to be Poole Frenkel type.

Kushwaha et.al. [97] performed the high field conduction studies in Se\(_{80-x}\)Te\(_{20}\)Sb\(_x\) thin films in dark and in the presence of light. At low electric fields ohmic behaviour was observed while at high electric fields the behaviour was found to be superohmic. They have explained their observed data on the basis of Poole Frenkel type conduction mechanism at high fields.

From the above discussion it is clear that Se-Ge and Se-Te based alloys are of considerable interest from the application point of view. Therefore study of electrical and photo-electrical properties of disordered materials has been the subject of extensive investigations for the best part of the century.

Inspite of large number of applications, fundamentally, the understanding of these materials is yet not complete. The analysis of disordered systems is complicated because of their complex structure and diverse nature of electrical and photo-electrical properties. A systematic study of electrical and photo-electrical properties provides useful information about the band gap, density of states, mechanism of conduction, type of dominant charge carriers, recombination kinetics and defect states etc. of the material.

Therefore, still much have to be done in this direction in order to completely understand the conduction mechanism prevailing in the chalcogenide glasses. Since the DOS in the mobility gap controls many physical properties of amorphous semiconductors, the determination of the
density of such states has become an important issue in these materials. The work by different authors also reveal the fact that SCLC have been an established tool to find DOS in chalcogenide glasses because it is relatively simple to measure and could potentially yield bulk DOS near Fermi level. The SCLC measurement and analysis constitute a relatively simple, straightforward and generally applicable method of obtaining the density of states in the gap of amorphous glassy chalcogenides. The present work is an attempt to measure the DOS by using SCLC technique in vacuum deposited thin films of some Se-Ge and Se-Te based chalcogenide glasses with an emphasis on preparation of those compositions which have relatively lower DOS so that one could potentially use them in various solid state devices. Photoconductivity measurements have also been tried in some of the photosensitive compositions to have better understanding regarding the above.

**Chapter 2** of the thesis deals with the experimental procedure adopted to make the glassy systems used in the present study. Experimental details of sample preparation and characterization have been presented in this chapter. The details of sample holder used have also been given in the chapter.

**Chapter 3** of the thesis reports the electrical properties of a-Se-Ge-M (M = Sn, Pb, Cu and Bi) glassy alloys. This chapter begins with the little introduction about the aforesaid glasses. A complete theory of high field conduction has been given in this chapter. DC Conductivity measurements have been presented. The effect of impurities (Sn, Pb, Cu and Bi) on the electrical properties of a-Ge$_{20}$Se$_{80}$ thin films have been carried out and discussed in this chapter.
The work done in this chapter has been published in the following journals:


Chapter 4 of the thesis reports the electrical properties of Se-Te-Sb glassy alloy. Effect of Sb on the electrical properties of a-Se\(_{80}\)Te\(_{20}\) thin films has been discussed. The data recorded for the DC Conductivity measurements as well as High field conduction measurements are presented and discussed in this chapter.

Chapter 5 of the thesis reports photoconductivity measurements in some selected (Se-Ge-Bi and Se-Te-Sb) compositions of the glassy alloys. The detailed theory related to the above has been also given in this chapter. The steady state and transient photoconductivity measurements in amorphous thin films of a-(Ge\(_{20}\)Se\(_{80}\))\(_{100-x}\)Bi\(_x\) and a-Se\(_{80-x}\)Te\(_{20}\)Sb\(_x\) glassy system with x = 2, 4, 6 and 10 prepared by vacuum evaporation technique have been studied. Temperature dependence of steady state photoconductivity is studied at different light intensities. Intensity dependence of photoconductivity, rise and decay of photoconductivity is studied at different fixed temperatures. The observed data are analyzed in the light of the existing theory.
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