CHAPTER - I
CHAPTER – ONE

INTRODUCTION TO CHALCOGENIDE GLASSES

1.1 Introduction

We live in an electronic era of technological advances based to a large extent on crystalline semiconductor devices. The marvels of modern semiconductor technology follow from sound physical knowledge and metallurgical control of single crystal materials. We have been the witnesses of a rapid development of science and technology based firstly on germanium, then on silicon, and later on GaAs crystalline materials.

The necessity to save weight and size, and to improve the speed in the function of the devices, stimulated an intense research activity with the purpose to reach the nanometer size field. In the same time the worldwide interest was moved from electronic to more complex optoelectronic applications.

Taking into account these big tasks of the 21st century, the class of materials must be enlarged. New materials with new properties must be prepared. It is remarkable, that, starting with 60 a new competitor appeared on the market of materials with implications in optics, electronics and optoelectronics: the disordered, amorphous or glassy materials.
The science of glass developed step by step. New classes of materials have been discovered. The first one was the large class of chalcogenides, materials that contain one or more chalcogen elements: sulphur, selenium, and tellurium. In the same time a young and clever researcher Ovshinsky [1], who founded his own company in USA, Energy Conversion Devices Inc. invented the first switching device based on a chalcogenide complex material. The search for new chalcogenide materials, phenomena and applications became a race, similar to the race for gold in the America of the 18-th century. Following the development of the glassy chalcogenide field, new optoelectronic materials based on halides have been discovered. Complex oxide and non-oxide glasses have been prepared and investigated in the last several decades, thus widening the groups of materials used in various optical, electronic and optoelectronic glasses. The great advantages of the disordered materials are: simple preparation procedures, low sensitivity to impurities, low cost, and, last but not least, the possibility to produce large area films of various thickness in classical systems for deposition: systems for evaporation in vacuum, magnetron systems, flash, spin-coating systems, sol-gel systems etc. In this thesis, I try to show the extent of the specific phenomena observed in chalcogenide glasses that makes these materials of large use and great perspective in electronics and optoelectronics.
A variety of stable glasses can be prepared in bulk, fiber, thin film, and multilayer forms using melt quenching, vacuum deposition, and other less common techniques. The atomic bonding structure in chalcogenide glasses is, in general, more rigid than that of organic polymers and more flexible than that of oxide glasses. Accordingly, the glass transition temperatures and elastic properties lie in between those of these materials. Some chalcogenide glasses containing silver and so forth behave as (super-) ionic conductors.

These glasses also behave as semiconductors or, more strictly, they are a kind of amorphous semiconductor with bandgap energies of 1-3 eV. Electronic properties, which are governed by the species of chalcogen atoms, are modified by disordered structures, while the relationship between the structure and electronic properties remains to be studied.

1.2. Structure of the chalcogenide glasses

Glass formation of chalcogenide materials is relatively easy, and many kinds of glasses have been prepared by means of melt quenching, vacuum deposition, and other less common methods such as spin coating and mechanical amorphization [2-7]. Among the glasses, only selenium vitrifies as an elemental glass which is fairly stable at room temperature. Most of the stable binary glasses are compounds of a chalcogen atom and a group IV or V atom, such as Ge-Se and As-S, where atomic ratios can be varied widely. Ternary and more complicated
glasses are of various kinds; these can probably be prepared by alloying with any kind of atom, including cations such as sodium and metallic atoms such as erbium, although the concentration may be limited. Oxychalcogenide and chalcohalide glasses can also be synthesized. Thermal stability depends upon the glass. When heated, stable glasses such as As₂S₃ exhibit only the glass transition, some glasses such as selenium undergo glass transition and crystallization, and tellurium glasses are likely to crystallize directly. As shown by the horizontal sequence in (Figure - I), chalcogenide glasses tend to possess properties intermediate between those of organic polymers and oxide glasses. (Table - 1) lists examples of elastic and thermal properties. On the other hand, chalcogenide glasses are denser than polymers and oxide glasses, since they are composed of heavier elements (S, Se, Te) than those (H, C, Si, O) in the others.

Chalcogenide glasses bear some similarity to oxide glasses, since both oxygen and chalcogens belong to group VI in the periodic table. The valence-electron configuration of all these elements is s²p⁴, and two p-electrons form atomic bonds with two neighboring atoms (Figure. 2 and 3). An exception is cationchalcogen glasses.

However, in more detail, there exist marked differences between chalcogenide and oxide glasses, among which the most essential may be the ionicity of atomic bonds. For instance, according to Pauling's scale, As-Se and Si-
Table 1

Comparison of the density $\rho$, the bulk modulus $B$, the glass transition temperature $T_g$, thermal conductivity $K$, and the linear thermal expansion coefficient $\beta$ in polyethylene $\text{As}_2\text{S}_3$ and $\text{SiO}_2$. The thermal conductivity of $\text{As}_2\text{S}_3$ differs among reports.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$B$ (10$^{-10}$ N m$^{-2}$)</th>
<th>$T_g$ (K)</th>
<th>$K$ (W m$^{-2}$ K$^{-1}$)</th>
<th>$\beta$ (10$^{-5}$ K$^{-1}$)</th>
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<tbody>
<tr>
<td>Polyethylene</td>
<td>0.95</td>
<td>$\sim$ 0.2</td>
<td>150</td>
<td>0.4</td>
<td>15</td>
</tr>
<tr>
<td>$\text{As}_2\text{S}_3$</td>
<td>3.2</td>
<td>1.25</td>
<td>460</td>
<td>0.2-0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>2.2</td>
<td>3.65</td>
<td>1450</td>
<td>1.4</td>
<td>0.055</td>
</tr>
</tbody>
</table>
Figure 1 Characterization of chalcogenide glasses and semiconductors in comparison with other materials
Figure 2 Illustration of atomic structures in Se. Atoms are shown only for one chain.
Figure 3 Illustration of atomic structures in As$_2$S$_3$. The threefold and the twofold coordinated circles represent As and Se atoms, and the disordered layers consist of atomic clusters.
O possess bond ionicities of 0.4 and 1.7. Taking the ionicity of Na-Cl of 2.1 into account, we can regard chalcogenide glasses as being covalent and oxides as ionic.

The difference in the ionicity causes different bonding angles [4-6]. In the chalcogenide glass, for example in As$_2$Se$_3$, As-Se-As forms an angle of about 100$^\circ$, which seems to be governed by covalent p-electron orbitals (Figure - 3). In contrast, in SiO$_2$ the Si-O-Si bond angle is distributed around 150$^\circ$, which may be substantially influenced by Coulombic repulsive forces between positively charged silicon atoms. Hence, in As$_2$Se$_3$, AsSe$_3$ pyramidal units can be edge-shared (Figure - 3), while in SiO$_2$ only corner-sharing of SiO$_3$ tetrahedral units is permitted (Figure - 4). The coordination number, bond length, and bond angle specify the short-range structure up to the second-nearest neighbor atoms, which is nearly the same as that in the corresponding crystal.

The structure beyond the third-nearest neighbors, the so-called medium-range structure, remains controversial [2, 4, 6, 8]. Here one may envisage distorted quasicrystalline structures (Figure - 4), or otherwise, we may assume three-dimensional continuous random network structures, which were originally proposed for SiO$_2$ glass (Figure - 4). In other words, the former emphasizes a structural similarity to the corresponding crystal, and the latter universality in glass structures. The structural controversy may be less serious for selenium [4, 6]. The material is known to be composed of entangled chains and or ring molecules.
Figure 4 Illustration of atomic structures of SiO$_2$. The tetrahedral represent SiO$_{4/2}$ units.
(Figure - 5), depending upon the preparation conditions. Such structures are
typical of organic polymers such as polyethylene and, because of this
resemblance, amorphous selenium can be referred to as an "inorganic polymer".

In covalent chalcogenide glasses, as illustrated in (Figure - 6), it has
been argued that there exist some transitions at \( \langle N \rangle = 2.4 \) and 2.67 [4, 9]. Here,
\( \langle N \rangle \) is the average coordination number of atoms, which is defined as
\[ \langle N \rangle = \sum x_i N_i \]
where \( x_i \) is the atomic fraction (\( \sum x_i = 1 \)) of constituent elements and
\( N_i \) is the atomic coordination number, which is 2 for chalcogens (Figure - 2 and
Figure - 3).

Phillips and Thorpe have interpreted the transition at 2.4 as follows
[9]. In a glass with \( \langle N \rangle < 2.4 \), the structure is Floppy, and there exist so called
zero-frequency vibrational modes. That is, supposing only the bond length and the
bond angle provide structural constraints, there remain free (zero frequency)
vibrational modes. At \( \langle N \rangle = 2.4 \), the structure becomes just rigid, and stable
glasses can be prepared. Above this point, the structure is over constrained, and
glass formation becomes difficult.

However, the compositional dependence of some physical properties
such as the density and the optical energy gap manifest extrema and/or thresholds
also at \( \langle N \rangle = 2.67 \) [9]. Tanaka assumes that this is a signature of a topological
<table>
<thead>
<tr>
<th>Structure</th>
<th>Electron distribution</th>
<th>Energy level atom</th>
<th>Energy level solid</th>
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<tr>
<td>Se</td>
<td><img src="image" alt="Se structure" /></td>
<td><img src="image" alt="Se electron distribution" /></td>
<td><img src="image" alt="Se energy levels" /></td>
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<tr>
<td>Si</td>
<td><img src="image" alt="Si structure" /></td>
<td><img src="image" alt="Si electron distribution" /></td>
<td><img src="image" alt="Si energy levels" /></td>
</tr>
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</table>

**Figure 5** Comparison of a-Se and a-Si the micro structure, the valance electron distribution around an atom, and electronic structures in an atom and the solid.
Figure 6 A schematic composition dependence of some properties as a function of the average coordination number $<N>$. Type (a) includes the position of the first sharp X-ray diffraction peak and the glass transition temperature. Type (b) includes the band gap energy, the specific volume, the specific heat, and the thermal expansion coefficient. Type (c) includes the elastic constant and the density of the tunneling states. Type (d) includes the intensity of the first sharp X-ray diffraction peak and the photodarkening effect.
phase transition from two-dimensional (< 2.67) to three-dimensional (< 2.67) structures. As illustrated in (Figure - 7), however, some physical properties such as the glass-transition temperature increase monotonically with $\langle N \rangle$. Further compositional studies are needed to obtain universal insights. It should be noted that such $\langle N \rangle$ dependence studies are inherent to covalent glasses, which can be varied continuously in atomic compositions. On the other hand, with the vertical change in the periodic table from sulphur to selenium and tellurium, the atomic bond becomes more metallic [3,6]. Directional bonding character changes to fairly isotropic in tellurium alloys, which are then likely to undergo crystallization relatively easily. The glass becomes darker in color, and the electrical conductivity becomes higher.

Chalcogenide glasses containing group I -III atoms are exceptional from the above descriptions [6]. These atoms are likely to behave as cations, which add some specific features. For instance, in Cu-As-Se, it has been demonstrated that the coordination number of selenium increases from 2 to 4. It is also known that in the Cu-As-Se system, glass formation is possible along the line connecting As$_2$Se$_3$ and Cu$_2$Se. This glass-formation region has been interpreted by Taylor et al. [10] using a formal valence shell model, which assumes that lone-pair electrons are transferred to bonding electrons with compositional changes. Another prominent feature, which should be pointed out here, is the ionic
Figure 7 Raman scattering spectra of As$_2$S$_3$ in (a) an as evaporated film and (b) a melt quenched bulk glass. For comparison, a spectrum of the crystalline form is also shown in (c).
conduction in some glasses containing lithium, sodium, and silver [3,6,11]. In these glasses, the ion forms atomic bonds with chalcogen atoms with relatively long bond distances of 0.25-0.3 nm. This feature and the high dielectric constant ($\varepsilon$, $\approx$ 10) in chalcogenide glasses favor marked ionic conductivity, since coulombic attractive forces are suppressed and the ions can move easily. Several glasses, such as Li$_2$S-P$_2$S$_3$-LiI, exhibit superionic conduction of $10^{-3}$ S cm$^{-1}$ at room temperature. In contrast to the electronic conduction, the ionic conduction tends to be enhanced with structural disordering [11,12]. For instance, the Ag$^+$ conductivities in crystalline and glassy AgAsS$_2$ are reported to be $10^{-7}$ and $10^5$ S cm$^{-1}$.

Finally, it should be noted that the atomic structure and related properties in chalcogenide glasses depend upon preparation methods and history after preparation [6,11]. This prehistory dependence is common to all non-equilibrium systems, such as glass. For instance, as shown in (Figure - 7), Raman scattering spectra of As$_2$S$_3$ depend considerably upon the preparation methods.

### 1.3 Electronic Structure of Chalcogenide Glasses:

Chalcogenide glasses possess electrical and optical bandgaps of 1-3 eV and accordingly they can be regarded as amorphous semiconductors. The gap decreases in the sequence of sulphur, selenium, and tellurium, reflecting the enhanced metallic character. On the other hand, polyethylene and SiO$_2$ are
insulators with energy gaps of 5-10 eV and accordingly these are transparent at visible wavelengths (Figure - 8). As a semiconductor, the overall property of chalcogenide glasses can be grasped as the vertical sequence in (Figure - 1). That is, with the change from organic semiconductors such as polyvinyl-carbazole, chalcogenides, hydrogenated amorphous silicon films, to crystalline semiconductors, the electronic mobility becomes higher and a faster response is available. The material also becomes more rigid. Instead, material prices seem to increase with this sequence, which may reflect their typical preparation methods, i.e., coating, evaporation, glow discharge, and crystal-growth techniques, respectively.

As exemplified in (Figure - 5), the electronic structure of a chalcogenide glass is essentially the same as that of the corresponding crystal [6,11,13]. That is, in covalent glasses with the chalcogen coordination number of 2, the top of the valence band is composed of lone-pair p-electrons of chalcogen atoms, and the bottom of the conduction band is composed of anti-bonding states of covalent bonds. The bandgap energy is similar (~ ± 10%) to that in the corresponding crystal.

Due to this nature of the valence band, dramatic effects of pressure upon electronic properties appear [8,11]. Hydrostatic compression preferentially
Figure 8 Optical absorption spectra of As$_2$S$_3$ (solid line) and SiO$_2$ (dotted line) glasses.
contracts the intermolecular distance of $\sim 0.5$ nm, and then the overlapping between lone-pair (Figure 2).

Electrically, however, glasses exhibit smaller conductivities than the corresponding crystals [3, 4, 6, 12]. This is because the electronic mobility is suppressed by bandtail and gap states, which are manifestations of disordered structures. Specifically, sulfide glasses such as $\text{As}_2\text{S}_3$ and $\text{GeS}_2$ behave as insulators, the conductivity being smaller than $10^{-15}$ S cm$^{-1}$. On the other hand, the carrier density of intrinsic semiconductors is governed by the bandgap energy, and accordingly it is assumed to be similar to that in the corresponding crystal.

In detail, the glass can be regarded as a p-type semiconductor or, more exactly, hole conduction is greater than electron conduction [3,4,13,14]. The reason has not been elucidated. In selenium at room temperature, holes exhibit conventional Gaussian transport with a mobility of $0.1$ cm$^2$ (Vs)$^{-1}$. However, at low temperatures and, in several materials, at room temperature, holes exhibit so-called dispersive transport, and the effective mobility decreases to $10^{-5}$ cm$^2$ (Vs)$^{-1}$ or even less. Such hole motions are described in terms of multiple trapping with band-tail states or hopping transport in gap states. In general, the position of the Fermi energy, which may be located near the center of the bandgap, cannot be controlled by impurity doping.
However, there are a few exceptions, such as Bi-Ge-Se and Pb-In-Se, in which the thermopower indicates n-type conduction [3,13] Hosono et al. [15] have discovered a high n-type conductivity of $10^{-2}$ S cm$^{-1}$ in amorphous Cd-In-S films. In these films, sulphur atoms seem to be fourfold coordinated, as in crystalline CdS.

Optically, as shown in (Figure - 8), chalcogenide glasses are transparent between red (or near IR) and IR regions [3, 4, 6, 13]. The short-wavelength cutoff is determined by electronic excitation, and the long-wavelength limit by atomic vibrations; this feature is common in semiconductors and insulators.

The electronic absorption edge consists of three spectral curves [4, 6, 13, 14]. In the absorption region higher than $\sim 10^3$ cm$^{-1}$, the absorption spectrum $\alpha(hv)$ in many materials follows the functional dependence $(\alpha hv)^{1/2} \propto hv - E_g^T$, and the optical bandgap energy is defined conventionally using $E_g^T$, the so-called Tauc gap. For smaller absorption coefficients, a temperature independent Urbach tail with the form $\alpha \propto \exp((hv/E_v))$ is observed, where $E_v$ is the Urbach energy. Selenium is exceptional here, for which $E_v$ is markedly temperature dependent.

Interestingly, for chalcogenides, $E_u \approx 50 \text{meV}$ which is comparable with $E_u \approx 50 \text{meV}$ in hydrogenated amorphous silicon. In the spectral region $\alpha \leq 10^6 \text{ cm}^{-1}$, a weak absorption tail with a dependence of $\alpha \propto \exp((hv/E_u))$ is
observed, where $E_o \approx 500 \text{meV}$ in As$_2$S$_3$. This absorption tail is influenced by impurities, but even in purified samples the tail still exists. It may be due to intrinsic mid-gap states. Interpretation of these spectral dependences still remains ambiguous.

Atomic structures responsible for the mid-gap states have not been experimentally confirmed, while the concepts, i.e., charged dangling bonds and/or valence alternation pairs, are frequently employed for the interpretation of many observations [4, 6, 14, 16, 13, 17]. The density of such native defects is estimated at $10^{15} - 10^{17}$ cm$^{-3}$ from considerations of the formation energy. For instance, the photoluminescence, which is excited by photons with $h\nu \approx E_o /2$ and which is emitted at $h\nu \approx E_o /2$, has been interpreted as a manifestation of structural transformations of these defects.

Photoelectrical properties of chalcogenide glasses have been studied extensively [6, 16, 13], probably because of their unique photoconductive applications. Specifically, amorphous selenium films deposited onto substrates held at 50 - 60°C are highly photoconductive, and the characteristics have been investigated extensively. Among many features examined, the one that is markedly different from that in conventional crystalline semiconductors is the existence of a "non-photoconducting spectral gap". The photoconductive spectral edges in amorphous selenium are blue-shifted by more than 0.5 eV from the
optical absorption edge. Geminaterecombination of photoexcited carriers, which suppresses photocurrents, is assumed to be responsible for the spectral gap. In addition, avalanche multiplication of photocreated carriers has been demonstrated in amorphous selenium. This phenomenon appears to be anomalous, since the disordered structure is assumed to be unfavorable for producing accelerated carriers, which can cause impact generation of other carriers. Chalcogenide glasses are known to exhibit prominent nonlinear optical effects [2,4,7]. (Table - 2) compares some nonlinear parameters of As$_2$S$_3$ and SiO$_2$ glasses. It can be seen that As$_2$S$_3$ is more efficient than SiO$_2$ by a factor of $10^2$.

1.4 Introduction to the thin film

The beginning of "Thin film science" can possibly be traced to the observations of Grove [18] who noted that metal films were formed by sputtering of cathodes with high energy positive ions. Since then it has come a long way and it is no longer a subject of some casual academic interest but has become a full fledged discipline. The phenomenal rise in thin film researches is, no doubt, due to their extensive applications in the diverse fields of electronics, optics, space science, aircrafts, defense and other industries. These investigations have led to numerous inventions in the forms of active devices and passive components, piezo-electric devices, micro-miniaturisation of power supply, rectification and amplification, sensor elements, storage of solar energy and its conversion to other
forms, magnetic memories, superconducting films, interference filters, reflecting and antireflection coatings and many others. The present developmental trend is towards newer types of devices, monolithic and hybrid circuits, field effect transistors (FET), metal oxide semiconductor transistors (MOST), sensors for different applications, switching devices, cryogenic applications, high density memory systems for computers, etc. Further, because of compactness, better performance and reliability coupled with the low cost of production and low package weight, thin film devices and components are preferred over their bulk counterparts. There has been a phenomenal increase in their applications which have outpaced the technology of production, development of newer types of materials and better processes for semi-conducting, dielectric and other films needed by various industries. Intensive investigations are going on not only in the field of basic thin film physics, but also in materials science, thin film circuit designs, production engineering concerning thin films, etc. to cope up the demand of industries. Film properties are also sensitive not only to their structures but also to many other parameters including their thickness especially in the thin film regions. Hence a stringent control of the latter is imperative for reproducible electronic, dielectric, optical and other properties. However, in this chapter only the use of films, their deposition technology and thickness measurement techniques etc. will be discussed in brief.
1.5 Nature Of Thin Film

The term 'thin film' has often been loosely used in literatures to imply not only a layer of a solid material but also of a liquid or a gaseous phase. However, all topics on thin films discussed in this thesis will be limited to solid films only. Further, there is neither any well-defined limit of its thickness to imply the end of the thin film stage nor one to indicate its transition to the thicker film region. All basic researches on thin films are generally confined to a limited range of thickness, say between a few Å to about 5000 Å depending on the properties to be investigated, whereas for technological applications where reliability of performance is the most important criterion, the thickness limit at the lower range is generally higher than 1000 Å and can be as high as 5-10 µm or even more. In order to cover this wide range of film thickness both for basic researches and applications, a "thin film" may be arbitrarily defined as a solid layer having a thickness varying from a few Å to about 10 µm or so. Since the thickness limitation is rather arbitrary, even somewhat thicker films may also come within the scope of the above definition. Within the connotation of thin film, often a further subdivision of thickness is made under the categories (i) ultra thin, (ii) thin (or very thin) and (iii) comparatively thicker ones, the last one generally being greater than 1000 Å. The categories (i) ranging from a few to about 50-100 Å and (ii) from about 100 Å to 1000 Å or less are all arbitrarily fixed for convenience.
and the transition regions from one category to the next one are not distinct at all:

It may be mentioned here that the above confusion in the nomenclature or definition of film thickness is further complicated by the coinage of a new term i.e., "thick films" which are of great practical importance. This new term indicates an entirely new class of films rather composite film layers obtained by the process of screen printing and subsequently firing a paste composed of a mixture of metals/alloys or oxide powder along with or without glass or ceramic particles suspended in some organic solvent vehicles and these films have thickness of about 10 µm and often more. The nature of these "thick films" which are used for printed circuits and for other purposes is quite different from the thin films we are going to consider here in the thesis.

Whatever be the film thickness limit, an ideal film can mathematically be detailed as a homogeneous solid material contained between two parallel planes and extended infinitely in two directions (say x, y) but restricted along the third direction (z), which is perpendicular to the x-y plane. The dimension along z-direction is known as the film thickness (d or t). Its magnitude may vary from a limit \( d \rightarrow 0 \) to any arbitrary value say to 10 µm or more but always remaining much less than those along the other two directions i.e. x and y. A real film, however, deviates considerably from the ideal case since its two surfaces are ever exactly parallel even when formed in the best experimental
deposition conditions and also the material contained between the two surfaces are rarely homogeneous, neither uniformly distributed nor of the same species. It is also a common experience that a film may also contain many imperfections, impurities, dislocations, grain boundaries and various other defects and may also be discontinuous. Further the top surface of a film often develops some topographical features and various characteristic of the growth conditions and these features are sometimes so prominent as to be visible even to naked eyes. Some of these features can, no doubt, be minimised by appropriate control of the deposition condition but cannot altogether be avoided. The bottom surface of a film in contact with a substrate generally takes up the topographical features of the latter.

Some of the factors which determine the physical, electrical, optical and other properties of a film are the following viz. rate of deposition, substrate temperature, environmental conditions, residual gas pressure in the system, purity of the material to be deposited, inclusion of foreign matter in the deposit, in homogeneity of the film, structural and compositional variations of the film in localised or wider areas etc. some of which have been actually observed [19 - 21]. A transition from the bulk to the thin film state may even cause a drastic change in its properties as illustrated by the behaviour of alkali metals and also noble metals. Thus highly conducting sodium, potassium rubidum, and also gold, platinum etc.
having positive temperature coefficient of resistance (TCR) in the bulk form show negative TCR when in thin film states thus behaving as semiconducting films. Bulk bismuth and antimony—which are metallic in nature behave as semiconductors in the thin film state [22]. Buckel and Hilsch [23] observed that thin bismuth films unlike bulk showed superconducting properties at low temperatures. Highly disordered or amorphous films have electrical or magnetic properties which may differ by several orders from that of the bulk single crystals.

All films whether prepared by vacuum deposition or by other technique are invariably associated with some growth defects or imperfections [24 - 27] such as lattice defects, stacking faults, twinning, disorders in atomic arrangement, dislocations, grain boundaries, foreign atom inclusion, etc. Surface states of a film also play a dominant role in modifying electrical and other properties. In addition because of a high surface to volume ratio in a film, a freshly formed film surface becomes highly reactive. Further because of the unbalancing of forces near the surface region, new phenomena such as thermionic emission, adsorption of gases, catalysts, solid state reactions; etc. characteristic of a surface are more often observed in thin films rather than in bulk. It is, therefore, of utmost importance to study thin films not only because of tremendous technological importance but also of our inadequate knowledge about their interactions with the electrical, magnetic and electromagnetic fields. There is often a considerable
deviation from that of the bulk-behaviour and sometimes new phenomena are observed in the thin film state. Further from these studies it may be possible in certain cases to predict their interactions with bulk materials.

1.6 Utility 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 thermal switch 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 photoconduction 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 [28] 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%.
Amorphous silicon solar cells have been produced commercially [29] 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 are 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. 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 and the electrical properties of the thin films of the chalcogenide glasses. Various properties have been described qualitatively. Emphasis has been given to optical electrical constants of these semiconductors which are most suitable for electronic devices.
REFERENCES


