Chapter 2
Experimental details

2.1 Introduction

Amorphous solids are characterized by short range ordered arrangement of atoms. These materials are metastable. The processes used in preparing these materials involve excess of free energy to be frozen in the system. Preparation of amorphous materials is much easier and cheaper in comparison to crystalline materials. These materials can readily be prepared from solid, liquid and vapor phases. All amorphous solids are thermodynamically unstable and they tend to relax in the metastable phase. The processes used in the preparation of amorphous materials allow short range atomic rearrangements which tend to minimize the concentration of defect centers and to provide long range strains. These materials can exist in various compositional and structural states each having different properties suited to specific practical applications. This property has proved useful for application of these materials in number of fields. It has been possible to make significant changes in their physical properties by controlling the short range order in them.

Chalcogenide glasses can exist in elemental, binary, ternary, quarternary and multicomponent forms. Classification of these materials is difficult in view of the freedom allowed in amorphous systems to depart from stoichiometric proportions of the constituents. In recent years, these glasses have drawn the attention of scientists and researchers worldwide because of their applications in number of fields like solar energy conversion [1], microlenses [2], optical mass memories [3], complex optical devices [4], fibre amplifiers and lasers [5, 6] etc. Since these materials are less sensitive to doping of impurities [7], therefore, highly sophisticated technology of fabrication is not required to fabricate these materials. Upon cooling a liquid below its melting point, it either crystallizes or form glass. For example, if molten selenium (Se) is rapidly cooled, the selenium thus obtained is amorphous in nature and it still retains semiconducting behaviour. The process of rapid cooling destroys the long-range order. These materials made by melt quenching technique are often referred to as glasses, because they exhibit the glass transition temperature ($T_g$). During the crystallization, the viscosity, entropy, volume and internal energy change discontinuously and the transformation is first-order. However, in glass formation these properties change continuously, although the change may be rapid in the
vicinity of $T_g$. The slower the rate of cooling, the larger is the region for which the liquid is supercooled and hence lower is the glass transition temperature. The $T_g$ of a particular material partly depends on its thermal history. The value of $T_g$ is influenced by the prevailing experimental conditions to a large extent, e.g. the cooling rate of the melt. When a liquid is cooled, either crystallization takes place at the melting point ($T_m$) or becomes supercooled for temperatures below $T_m$ and becomes more viscous with decreasing temperature. The crystallization process is manifested by an abrupt change in volume at $T_m$, whereas glass formation is characterized by a gradual break in slope. The region over which the change in slope occurs is the $T_g$. The transition to the glassy state is not continuous, so the $T_g$ is not well defined. The thermal expansion and heat capacity of the glassy state are generally observed to be close to the crystalline state. The transition from the crystalline state to glassy state [8] is shown in Fig. 2.1. Glass formation becomes more probable, when the cooling rate is greater, the sample volume is smaller and the crystallization rate is slower.

Figure 2.1: Schematic variation of volume with temperature for a glass forming material.

However, a fast quenching to avoid crystallization introduces excess volume which results in large density fluctuation and vice versa. A very slow cooling rate will
maximize the density and minimize strains, which increases the likelihood of nucleating crystals. So, actual preparation technique is always a compromise. The nature of $T_g$ is complex and even today it is poorly understood. Numerous studies have been devoted to the measurements and understanding of the glass transition temperature, which is influenced by experimental conditions, e.g. the cooling rate of liquid. Even for the measurements under standard conditions, there is no consensus as to which structural or thermodynamical factors are responsible for determining $T_g$. Tanaka [9] has discovered an empirical relationship between $T_g$ and the average coordination number per atom ($Z$) calculated in terms of the covalent bonding.

$$\ln T_g \equiv 1.6Z + 2.3$$

The ease of glass formation generally relates to the chemical or structural properties of the system, thermodynamic or free-volume aspects (average atomic coordination) and topology of the amorphous structure. Only those materials form glasses readily which possess an internal energy slightly larger in the amorphous state than in their crystalline states. The materials that inhibit crystallization on cooling a melt at a given composition for a liquid alloy favour the glass formation more, as the rate of crystallite nucleation and growth at that composition reduces. The alloys of chalcogenide glasses have a certain range of atomic percentages of each constituent in which they can be glassy, beyond this range, they are either semicrystalline or crystalline.

### 2.2 Preparation of Chalcogenide Glasses

Most of the Chalcogenide exist in metastable state i.e. state in which the solid does not have the lowest possible free energy for its particular temperature and pressure but additional energy is necessary to attain equilibrium. These materials can be prepared by number of methods like thermal quenching of melt, glow-discharge decomposition of a gas, Rf sputtering and vacuum evaporation. These techniques are designed to make short-range atomic arrangement. The formation of glasses requires prevention of crystallization and the growth processes, which are responsible for crystallization. The cooling required in quenching depends upon the system, which one wants to prepare.

The author has used melt-quenching technique to prepare various samples of chalcogenide semiconductors. The apparatus used for the preparation of materials
consist of a furnace to prepare the melt of the mixture, rocking arrangement to make the melt homogeneous and a quenching arrangement to cool the melt. The furnace used for melting the mixture consists of winding of 60 turns of 1mm diameter canthal wire over a hollow silica tube of internal diameter 8 cm and length 22 cm. The wire wound tube is encased inside an aluminum cover (22 cm x 16 cm) and the annular space is packed with asbestos powder for insulation. The whole assembly is covered with asbestos sheets, leaving an opening (diameter 3 cm) on either side for the insertion of the ceramic rod to which quartz ampoules are fastened. Furnace is operated up to maximum of 120 V ac. The maximum temperature that can be maintained inside the furnace is 1200 °C. The whole arrangement is depicted in the Fig. 2.2. The pulleys shown in the figure operates with the help of a motor.

![Schematic diagram of the rocking furnace.](image)

Materials are prepared by taking constituent elements of purity 99.999 % in required atomic weight percentages. The electronic balance used for these measurements has an accuracy of 0.0001 gm. Table 2.1 represents the method used to calculate the stoichiometric weight of the various constituents of a sample of $M_x\text{Se}_{1-x}$ (M=In, Ga, Sb), $x = 0.4, 0.5, 0.6, 0.7$. The weighed materials are then mixed together
and sealed in quartz ampoules (length ~ 12 cm, internal diameter ~ 0.8 cm, outer
diameter ~ 1.0 cm) under a pressure of ~ 10⁻⁵ mbar using the diffusion pump (M/s
Hind High Vacuum (HHV); Model: VS-65D). Then the ampoules are kept inside
rocking furnace at temperature of the constituent element having highest melting
point for nearly 24 hours. The rocking is done to make the melt homogeneous. Then
the quartz ampoules are quenched in liquid nitrogen or ice water. The glassy materials
in the form of ingots were obtained by breaking the quartz tubes. The amorphous
nature of the materials is verified by X-ray diffraction (XRD) method (PANalytical
X’Pert PRO X-ray diffractometer). The absence of any prominent peak in some
samples confirmed the amorphous nature. However, in samples, we have got a peak
which confirms the crystalline nature of the samples.

Table 2.1: The stoichiometric weight of the various constituents of \( M_x Se_{1-x} \)
\( (M=\text{In}, \text{Ga}, \text{Sb}), x = 0.4, 0.5, 0.6, 0.7. \)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Atomic weight</th>
<th>Density gm/cm³</th>
<th>Alloy</th>
<th>Percentage</th>
<th>Density gm/cm³</th>
<th>Weight (3gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>78.96</td>
<td>4.82</td>
<td>( \text{In}_2\text{Se}_3 ) %40-%60</td>
<td>5.816</td>
<td>1.4761</td>
<td>1.523</td>
</tr>
<tr>
<td></td>
<td>114.81</td>
<td>7.31</td>
<td>( \text{InSe} ) %50-%50</td>
<td>6.065</td>
<td>1.777</td>
<td>1.222</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \text{In}_3\text{Se}_2 ) %60-%40</td>
<td>6.314</td>
<td>2.057</td>
<td>0.943</td>
</tr>
<tr>
<td>In</td>
<td>114.81</td>
<td>7.31</td>
<td>( \text{Ga}_2\text{Se}_3 ) %40-%60</td>
<td>5.253</td>
<td>1.111</td>
<td>1.888</td>
</tr>
<tr>
<td></td>
<td>69.72</td>
<td>5.904</td>
<td>( \text{GaSe} ) %50-%50</td>
<td>5.362</td>
<td>1.406</td>
<td>1.593</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \text{Ga}_3\text{Se}_2 ) %60-%40</td>
<td>5.470</td>
<td>1.709</td>
<td>1.290</td>
</tr>
<tr>
<td>Ga</td>
<td>69.72</td>
<td>5.904</td>
<td>( \text{Ga}_7\text{Se}_3 ) %70-%30</td>
<td>5.578</td>
<td>2.019</td>
<td>0.980</td>
</tr>
<tr>
<td>Sb</td>
<td>121.76</td>
<td>6.697</td>
<td>( \text{Sb}_2\text{Se}_3 ) %40-%60</td>
<td>5.571</td>
<td>1.520</td>
<td>1.479</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \text{SbSe} ) %50-%50</td>
<td>5.758</td>
<td>1.819</td>
<td>1.180</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \text{Sb}_3\text{Se}_2 ) %60-%40</td>
<td>5.946</td>
<td>2.094</td>
<td>0.905</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \text{Sb}_7\text{Se}_3 ) %70-%30</td>
<td>6.134</td>
<td>2.347</td>
<td>0.652</td>
</tr>
</tbody>
</table>
2.3 Preparation of Thin Films

Thin films can be prepared by number of methods. These methods can be divided into two groups: Physical method and Chemical method. In physical method, materials are physically evaporated whereas in chemical method there is chemical separation of ions. Physical methods for thin film deposition are vacuum evaporation [10-12], electron-beam evaporation [13], RF sputtering [14], ion beam evaporation [15]. Some of the chemical methods for thin film deposition are chemical bath deposition [16], chemical vapor deposition [17], cathode electrolytic deposition [18] etc.

Thermal evaporation method has been used by the author to prepare thin films of these materials. Ideal conditions required in preparation of thin films by thermal evaporation are high vacuum, pure starting material, a large source-to-substrate separation (to achieve normal incidence), a fairly slow evaporation rate, and ultra clean smooth substrates. Optical and electrical properties of thin films are dependent on the deposition parameters. Thus, thin film deposition is very important from technological point of view.

Substrate used for thin film deposition is 7059 Corning glass (dimensions: 2.5 cm x 2.5 cm). The conductivity of the glass (substrate) is very low (~$10^{14}$ $\Omega^{-1}$ cm$^{-1}$). Cleaning of the substrate used in thin film deposition is very important. If the substrate is contaminated with impurities, then there is tendency of film to crack. Thus, it is necessary for the substrates to be cleaned before deposition very carefully. Substrates are first cleaned by soap solution and then by vapor cleaning. Soap solution removes the oil or dust impurities present on the substrates. Then substrates are cleaned by vapor cleaning method. In vapor cleaning, first acetone vapors are used to remove organic impurities and then methanol vapors are used to remove inorganic impurities.

Cleaned substrates are placed in thin film coating unit. The coating unit is cleaned with acetone and methanol prior to every deposition. A diffusion pump (M/s Hind High Vacuum (HHV); Model: VS-65D) is used to maintain vacuum in the coating unit ($\approx 2 \times 10^{-5}$ mbar). The coating unit consists of two copper electrodes. Weighted materials are placed in the Tungsten or Molybdenum boat connected between the two copper electrodes. Tungsten boat is used because it has very high melting point. A high current is passed through the boat by connecting the copper electrodes with high current low voltage source. Substrates are placed at some height (~16 cm) above the tungsten boat. The films are kept in the deposition chamber in dark for 24 hours before mounting them in a metallic sample holder to attain thermodynamic equilibrium. Schematic diagram of
the thin film coating unit is shown in Fig. 2.3. Thickness of the sample is calculated using transmission method. The deposition parameters are kept identical for all alloys to make comparison of their properties.

Figure 2.3: Schematic diagram of the thin film coating unit used to deposit the thin films
2.4 Characterization of the Thin Films

2.4.1 X-Ray Diffraction

The bulk and thin films of the amorphous and crystal samples are characterized for their nature using the X-ray diffraction (XRD) method. A mask is used to carry out the XRD analysis on the thin films of the samples under investigation. In XRD, each atom becomes the source of scattered X-ray radiation. The scattered radiation from all the atoms of amorphous material will combine destructively as they fall on top of one another in the random manner. However, in the case of perfect crystal, the X-rays scatter without the loss of energy and constructive interference may occur. Absence of prominent peaks confirmed the amorphous nature of the thin films for different amorphous alloys prepared by melt quenching technique.

We use PANalytical X'Pert PRO X-ray diffractometer. It contains of PIXcel, PANalytical's 2nd generation solid-state detection technology, XRD Glass X-ray Tube, Cu source with wavelength 1.54 Å and power generation 35mA, 40KV. The Bragg law is the cornerstone of X-ray diffraction analysis, which allows us to make accurate quantification of the results of experiments carried out to determine crystal structure. It was formulated in 1912 by W. L. Bragg, in order to explain the observed phenomenon that crystals only reflect X-rays at certain angles of incidence. An X-ray incident upon a sample will either be transmitted, in which case it will continue along its original direction, or it will be scattered by the electrons of the atoms in the material. In general, the scattered waves destructively interfere with each other, with the exception of special orientations at which Bragg's law Eq (2.2) is satisfied. A Bragg condition is such that the scattered rays from two parallel planes interact with each other in such a way as to create constructive interference as shown in Fig. 2.4.

\[ n\lambda = 2d \sin \theta \]  

\( n \) = is the order of the reflection, \( \lambda \) = wavelength of incident x-rays

\( \theta \) = angle of incidence, \( d \) = lattice spacing
2.4.2 Electrical Characterization

It is verified that the dark conductivity and photoconductivity behaviour in alloys of thin films is not affected by annealing the films at room temperature for times longer than twenty four hours [19]. The present measurements are found to be of the same nature in the films deposited in different runs. Therefore, the conclusion of the present work will not be much affected by the surface effects, as most of the explanations given are qualitative in nature. The deposition parameters are kept almost identical of binary systems, so that a comparison of the results could be made for almost identical conditions. Some of the electrical properties, e.g. temperature dependence of dc conductivity and Hall Effect are measured on the thin films of the amorphous and crystal alloys. It is found that the magnitude of the dc conductivity and activation energy for dc conduction and Hall Effect with carrier concentration and mobility is the same within the experimental error of thin films in the first time of prepared and after some time. This further ensured that the composition of the evaporated films is not very different from the corresponding amorphous alloy prepared by quenching technique.

2.4.2.1 DC conductivity measurements

DC conductivity in chalcogenide semiconductors has yielded valuable information about the transport mechanism [20]. The chalcogenide show activated temperature dependence conductivity according to the relation

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E / kT)$$  \hspace{1cm} (2.3)

where $\Delta E$ and $\sigma_0$ are the conductivity activation energy and pre-exponential factor respectively. From various experimental results, it is evident that conduction in these glasses occurs either in the extended states beyond the mobility edge or in the
localized states at the band edges [21]. Most of the materials exhibit variable range hopping conduction amongst the localized states near Fermi level. A large value of $\Delta E$ either suggests that conduction occurs in extended states beyond mobility edge or in localized states at the band edge. We have used wide range of temperature from low temperature $100K$ to up of room temperature $400K$ for the dc conductivity measurements. Activation energy is calculated from the slope of $\ln \sigma$ vs $1000/T$ curves. DC conductivity ($\sigma$) of our thin films has been calculated at wide range of temperature using equation:

$$\sigma = \frac{L}{RA}$$

(2.4)

where, $R$ is the resistance of the film, $L$ is distance between the electrodes, $A$ is the area of film between the electrodes. Area of film is given by

$$A = bt$$

(2.5)

where, $b$ is length and $t$ is the thickness of the thin film.

**Design and Fabrication of a Sample Holder**

To carry out the various electrical measurements on the thin films at low and high temperatures, a specially designed metallic (stainless steel and brass) sample holder is fabricated in the laboratory. The detailed diagram of the sample holder is shown in the Fig. 2.5. Stainless steel is used to take care of the surface currents and unwanted disturbances in the measurements of small currents [picoamperes (pA)]. It also helps to provide proper shielding to the thin film samples for accurate current measurements.

During various experimental observations, at low and high temperatures, stainless steel is highly durable and corrosion-free. The sample holder is fitted with platinum sensor using teflon feed through. During different measurements, this Pt-sensor gives the exact temperature reading from $100K$ to $400K$ to which the thin film is subjected. The Pt-sensor is placed on copper block over another glass substrate very near to the thin film so that the chances of error in temperature measurement are very small. The other end of this copper block holder dimensions $(5cm \times 7cm \times 0.5 cm)$ is in direct contact with liquid nitrogen. By this arrangement, the temperature gradient is very small between the copper block and the liquid nitrogen filled in the sample holder.
Teflon feed through Stainless Steel Vacuum Gauge

Copper finger Heater 65 W Thin film on glass Pt-sensor

Figure 2.5: Stainless steel metallic sample holder optical and electrical measurements
A small circular glass window is made in the sample holder directly in front of the copper block on which the film is placed. The light is shone through this glass window to carry out the optical measurements on the thin films. The copper block from lower side is fitted with heater (65 watt) to anneal the thin films of various samples and to study their behaviour with rise in temperature. The rate is monitored through display of the digital panel meter which is connected to the Pt-sensor. The leakage current in the feed through (BNC connectors) is below the measuring range of the pico-ammeter.

2.4.2.2 Hall Effect measurements

When a semiconductor material, under electrical conduction, is subjected to a magnetic field, an electric field is developed. This electric field is perpendicular to the magnetic field and the current direction. The strength of the magnetic field depends upon the strength of the magnetic field and the current passing through the material. This effect is called Hall effect, named after its discoverer, E. H. Hall in 1879. This technique is widely used to quantify two parameters namely, carrier concentration (n or p) and mobility (µ). If a current I flows through a strip of thin film of rectangular cross section and if the strip is traversed by a magnetic field at right angles to the direction of the current, a voltage known as the Hall voltage, is produced between two superposed points on opposite sides of the strip, as shown in Fig. 2.6.

There is a linear relationship between the current I and the Hall voltage \( V_H \) with the direction of sample current and magnetic field as illustrated in Fig. 2.6. The charge carriers which produce the current are deflected towards the front edge of the sample. If the current is mainly due to electrons, the front edge becomes negatively charged whereas if the current is due to holes, it becomes positively charged. The conductivity \( \sigma \), carrier mobility \( \mu \), and the carrier concentration \( n \) are connected by a factor called the Hall coefficient \( R_H \):

\[
R_H = \frac{V_H d}{BI} \quad (2.6)
\]

\[
\mu_H = R_H \sigma_d \quad (2.7)
\]

\[
n = \frac{1}{eR_H} \quad (2.8)
\]

The conductivity of the sample at room temperature is calculated from the length, \( l \), of the sample, its cross-sectional area and its resistance, \( R_d \) using Eq (2.4). The magnetic field is measured by Hall Probe Gauss meter Model DGM102 and its value is 0.3T.
For measuring Hall voltage across the thin film we use Keithley 6517A and the current is supplied through digital power supply (Keithley 1-1200 volt).

2.4.3 Optical Characterization

Optical measurement of thin films is done by using the R. Swanepoel’s method [22] which is based on the approach of Manifacier et al. [23]. The transmission spectrum is obtained from visible-near Infrared (VIS/NIR) computer-controlled spectrophotometer [SOLAR-TII 2004]. The block diagram of spectrophotometer is shown in Fig. 2.7. The range for the transmission spectrum is taken from 400 nm to 1100 nm. The slit width of 1 nm is set in the spectrophotometer. Accuracy in the measurement of wavelength is 0.1 nm for VIS region and 0.2 nm for NIR region. The photometric accuracy is 0.2 % in the transmission measurements. Tungsten halogen lamp is used as optical source [Orial Company] with regulated power supply and control intensity of light.

Monochromator-spectrograph [SOLAR TII, MS 2004] is used to measure the transmission spectrum. Optical layout of monochromator-spectrograph is shown in Fig. 2.7. The light after passing through entrance slit and turning mirror is routed by collimator spherical mirror onto diffraction grating. Grating converts the parallel beam from each point of entrance slit into a fan of monochromatic parallel beams. Camera spherical mirror forms the monochromatic images of the entrance slit. These images, when combined, form a spectrum of a certain wavelength range. The light shutter shuts off the light passing through entrance slit. Diffraction grating is installed on a quadruple turret. The change of diffraction gratings is effected by turning the
turret at some angle around a particular axis. Flip mirror is used for the detector port selection. When the flip mirror is in position F, the axial port is selected as an exit port. When the flip mirror is brought to position F', the lateral port is selected as an exit port. MS 2004 is a completely automated device which uses an internal controller to control the operation of gratings (changeover and rotation), output mirror, entrance/exit slits, filter wheel and shutter. A Si-detector is mounted after the exit slit. The transmittance of the glass substrate with and without film is recorded. The transmission spectra of the film are obtained after subtracting the transmittance of substrate as reference. After passing through the sample compartment, the monochromatic beams are converged and then converted into an electric signal by the detector. The intensities of the two transmitted beams are electronically compared. The electric signal provided from the detector is processed by a CPU and the computational result is displayed directly on the CPU or output to recorder.

Figure 2.7: Optical layout of monochromator-spectrograph [SOLAR TII, MS 2004] used to measure the transmission spectra.
2.4.4 Time of Flight Technique

Transient Photoconductivity (TPC) or Time of Flight (TOF) techniques will be used to measure the carrier mobility in glassy semiconductor thin films [24-27]. In TOF technique, as shown in Fig. 2.8, we prepare two types of electrodes structure, sandwich structure and normal structure of our thin films. In first way, we deposit semiconductor thin film over pre-deposited aluminum, then semi-transparent aluminum electrodes above thin film and second way deposits thin film, then Al electrodes with 0.8 mm gap in the surface above it. The top electrode passes some amount of photons inside thin films by a short pulse of laser, Nd: YAG laser with $\lambda=1064$ nm, $\sim 10$ nsec pulse width and $\sim 10$ mJ power. Type of charge carriers (electrons or holes) are selected by applying a bias using regulated power supply. The current produced by the laser pulse in the presence of the applied electric field is recorded using digital storage oscilloscope (Velleman type PCS500; Interface software: PCLAB2000). From the shape of pulse we can found the charge carrier transit time ($T_t$), life time of carrier ($\tau$), rise time ($t_r$), fall time ($t_f$), using these parameters, has been calculated the mobility ($\mu$) from Eq (2.9).

$$u = \frac{d}{E \cdot T_t}$$  \hspace{1cm} (2.9)

where $d =$ thickness of thin film.

$E =$ applied field.

Figure 2.8: TOF Setup, normal and sandwich electrode structure.
2.4.5 Diode and Solar cell Characteristics

The samples of diode or solar cell consist of at least two layers to form a p-n junction. A diode is a p-n junction which measures the I-V characteristic and allows current conduction in the forward direction and blocks the current in the other (reverse) direction [28] as shown in Fig. 2.9

![Figure 2.9: Schematic diagram of p-n diode for I-V characteristics.](image)

The photoelectric effect is the basic physical process by which a photovoltaic cell converts sunlight into electricity. When light shines on a PV cell, it may be reflected, absorbed, or pass right through. But only the absorbed light generates electricity. Sandwiching these together creates a p-n junction at their interface, thereby, creating an electric field. A solar cell is a large-area p-n junction designed in such a way so as to allow the incidence of light in the semiconductor regions and produces current of the device as shown in the Fig. 2.10.

![Figure 2.10: Setup for solar cell testing.](image)
Bibliography


