Chapter 3

Experimental Details

This chapter includes a description of the experimental methods/techniques employed in the present work for the preparation of chalcogenide alloys in bulk and thin film form and their characterization by different techniques viz. X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX), UV–VIS–NIR spectroscopy, Electric conductivity and photoconductivity measurements.

3.1 Preparation of Bulk Samples

Chalcogenide compounds are generally prepared in vacuum at very low oxygen vapor pressure in order to prevent oxidation of constituent elements. These materials are moderate glass former depending upon their composition and thus require moderate to high quenching rates to quench the liquid melt into amorphous state. There are different techniques available for preventing crystallization of materials and thus obtaining amorphous state depending upon the nature of the materials. As example oxides of many elements can be found naturally in amorphous state or require low quenching rate for obtaining materials in amorphous state. On the other side metal can only be formed in amorphous state by quenching at very high rates and thus require special techniques (Splat quenching with cooling rates ~ $10^7$ K/sec). Chalcogenide materials can be made amorphous by quenching at moderate quenching rates and thus melt quenching is most suitable for preparing this class of materials in amorphous state. In this work, bulk samples of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x$ ($0 \leq x \leq 4$) were prepared by conventional melt quenching technique [Wang et al. (2004); Turnbull et al. (2004); Elliot (1990)]. In this technique quartz tube of internal diameter ~6mm and length ~100mm was first sealed from one end, necked down at a point near about the middle of tube by focused flame. The tube (ampoule) was then cleaned using Soap solution, Acetone, Aquaregia (1 part of Nitric acid + 3 Parts of HCl), HF and deionized water for 1h. The cleaned ampoule was dried in oven for 2–3h. Appropriate amount of constituent elements of 5N purity obtained from Sigma-Aldrich USA were weighed in electronic balance (make: Sartorious, model no. GC1603S–OCE) and poured in cleaned ampoule. These weighed materials were sealed in a quartz ampoule in a vacuum of ~$10^{-5}$ mbar. Utmost care has been taken while sealing the ampoule, since selenium has high vapor pressure and can react with...
oxygen and can burst the ampoule. Heating and mixing of the constituent elements was done in molten state in the evacuated and sealed ampoule. This was achieved by keeping ampoule in furnace and heating it at 4–5K/min heating rate upto 1373K for 72h. The ampoule was inverted at regular intervals (~1h) to ensure the homogenous mixing of the constituents, before quenching in an ice bath. The material was separated from the quartz ampoule by dissolving the ampoule into a solution of HF + H₂O₂ for approximately 48h. The obtained bulk is then powdered in motor pestle and this fine powdered material is used for further characterization of the material.

3.2 Density of Bulk Samples
The Archimedes method was used for the measurement of the density of as-prepared glasses. The weight of the piece of Se–Te–Ag glassy alloy was measured in air and in dibutyl phthalate using an electrical balance as w₁ and w₂ respectively, w₃ is the weight of the thread used for weighing the sample. The density of dibutyl phthalate (ρ(Dbρ)) is 1.05gcm⁻³ at 20°C. The density of the glassy alloy was calculated from the formula:

\[ \rho = \frac{w_1}{w_2 - w_3} \rho_{Dbp} \]  \hspace{1cm} (3.1)

3.3 Preparation of Thin Films
Optical properties of the chalcogenide glasses are studied by thin film preparation of the samples. 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. Some of the physical methods for thin film deposition are vacuum evaporation [Mitkova et al. (2004); Verlan (2003); Pattanaik and Srinivasan (2004)]. electron-beam evaporation [Kamboj et al. (2002)], rf sputtering [Balan et al. (2004)], ion beam evaporation [Mikhailov et al. (2000)] etc. Some of the chemical methods for thin film deposition are chemical bath deposition [Sandoval-Paz et al. (2005)], chemical vapour deposition [Nagels et al. (2003)], cathode electrolytic deposition [Gruszecki and Holmstrom (1998)] etc. Every deposition technique has its own advantages and disadvantages. The most commonly used technique for chalcogenide materials is thermal evaporation technique because of the fact that these materials have moderate
sublimation temperature. In this work author have used thermal evaporation technique for depositing \((\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x\) \((0 \leq x \leq 4)\) samples using Hind High Vacuum Coating Unit (model 12A4D). In this unit material to be deposited is kept in a boat shaped molybdenum sheet and tied to two ends of copper electrodes. The substrates are clamped with substrate holder with heating arrangement ~20cm directly above the molybdenum boat. The substrates used for depositing thin films were properly cleaned Corning glass slides. Cleaning of the slides can be done by similar way as we have explained earlier for ampoules. The coating chamber is cleaned with acetone prior to each deposition. Cleaned substrates are placed in thin film coating unit. A diffusion pump is used to maintain vacuum in the coating unit \((10^{-5}\text{ mbar})\). The coating unit consists of two copper electrodes. Weighted materials are placed in the molybdenum boat connected between the two copper electrodes. Molybdenum 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 ~ 12cm) above the molybdenum boat. The films are kept in the deposition chamber in dark for 24h before mounting them in a metallic sample holder to attain thermodynamic equilibrium. The deposition parameters are kept identical for all alloys to make comparison of their properties. The thickness of thin films was measured by KLA Tencor P15 surface profiler.

a) To study the effect of Ag addition on Se–Te glassy matrix (compositional dependence) thin films of thickness ~ 943 to 962nm were obtained.

b) To study the effect of thickness on \((\text{Se}_{80}\text{Te}_{20})_{96}\text{Ag}_4\) thin film. Thin films of thickness ~ 504 to 960nm were obtained.

c) Ultra thin films of thickness ~ 76 to 81nm were obtained.

3.4 Structure and Composition

X-rays interact with the electronic orbitals within an atom causing the incident X-ray photons to scatter. The penetrative power of the X-rays means that the photons can penetrate a large number of atomic layers, thus a large proportion of the scattered photons come from deep within the solid. Within a crystal, the regularly spaced atomic positions are repeated sequentially to form a superlattice. Each repetition forms a fundamental unit. Within the superlattice there are many possible planes of atoms. The
frequency at which an atom occurs is dependent on the plane angle of intersection. Therefore reflection of X-rays occurs from a very large number of atomic layers. Superposition of the wavelets from each atomic layer leads to interference fringes. For constructive interference, the wavelets must be in phase; hence the difference in path length between that traversed by a wavelet from different planes must be an integer number of wavelengths. This only occurs at specific angles. Deviating from these angles results in destructive interference and a sharp drop in the reflected intensity. The condition for high reflectivity is called Bragg’s Law and is given by following equation:

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

where \( d \) is the separation of the reflecting planes and is known as the lattice constant, \( \theta \) is the angle of the incident X-ray beam with respect the crystal planes, \( n \) is an integer corresponding to the number of wavelengths traversed between the atomic planes. So, by measuring the reflected intensity as a function of angle, a number of peaks will occur at different intensities corresponding to reflections from different crystallographic planes. From this data it is possible to calculate the structure of a crystal and the lattice spacings. For the diffraction measurements carried out in this thesis, two XRD systems have been used (i) Phillips PAN analytical system (ii) Shimadzu XRD–7000 system. Absence of prominent peaks confirmed the amorphous nature of the bulk and thin films.

EDX is an extremely powerful analytical technique of special value in conjunction with electron column instruments. In few seconds a qualitative survey of the elements present in almost any sample can be made, and in only a few minutes’ sufficient data can be collected for quantification. For this, a series of measurements are made in which the peak intensity from each element in the sample is compared to the peak intensity obtained from a reference standard using the same operating conditions. Sample dimensions are usually not a problem in an SEM. Most of the detectors used to date have been of the Si (Li) type, but with improvements in the processing methods of germanium, HPGe detectors may start impacting the market. The chemical composition of the obtained films is checked by EDX using SEM (JEOL) JSM–6610LV system and the gold coating has been done by Gold coater (JFC–1600). The elemental composition for each film (Se, Te and Ag) was measured at three different points and the average value was taken as the final composition.
3.5 Differential Scanning Calorimetry (DSC)

DSC is a technique we use to study what happens to glasses when they are heated. We use it to study the thermal transitions of glasses. Thermal transitions are the changes that take place in glasses when you heat it. The glass transition is also a thermal transition. DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. The thermal behaviour of the samples was investigated using Perkin Elmer (Pyris Diamond) DSC System. In each study approximately 10mg of the bulk material was used. DSC runs were taken for four different heating rates i.e., 5, 10, 15 and 20 K/min for each of the composition so as to get glass transition temperature ($T_g$), crystallization temperature ($T_c$), peak crystallization temperature ($T_p$) and melting temperature ($T_m$). All the DSC runs were performed under the liquid nitrogen atmosphere. The DSC instrument was calibrated with standard materials prior to the start of the experiment. Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs. As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature ($T_c$). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature ($T_m$). The melting process results in an endothermic peak in the DSC curve. The ability to determine transition temperatures and enthalpies makes DSC an invaluable tool in producing phase diagrams for various chemical systems. The apparent activation energies of glass transition and crystallization have been calculated from the heating rate dependence of $T_g$ and $T_p$ respectively.
The glass forming ability of the system is calculated which is very important and this is the area which is steadily evolving. The glass transition temperature is defined as the temperature corresponding to the intersection of two linear portions adjoining the transition elbow of DSC trace of first endothermic peak as shown in Figure 3.1. The $T_c$ is taken as the temperature corresponding to the onset of crystallization. The deconvolution of the broad exothermic peaks was carried out by using the Peak Fit v4.12 (SeaSolve, USA) software program. The DSC data for the exothermic peak was well fitted by using the Savitzky-Golay algorithm.

### 3.6 Optical Studies

The optical transmission and reflection spectrum was recorded at room temperature using:

a) UV-visible spectrophotometer (VARIAN Cary500 UV–VIS–NIR) in the wavelength range of 500–2500nm, in case of thin films of thickness ~ 943 to 962nm and ~ 504 to 960nm.

b) UV-visible double beam spectrophotometer (PerkinElmer LAMBDA 25UV/Vis Systems) in the wavelength range of 300–1100nm in case of thin films of thickness ~ 76 to 81nm (Ultra-thin films).

### 3.7 Electrical and Photoelectrical Studies

The dc conductivity measurements for thin films of thickness ~ 943 to 962nm were carried out in the temperature range 263–333K in a running vacuum of $10^{-5}$ mbar.
Electrical contacts with an electrode gap of ~2mm in a coplanar geometry were made using silver paint. For photoconductivity measurements the sample was mounted inside a metallic cryostat with a transparent window through which samples were illuminated. All the measurements were made in a vacuum of $\sim 10^{-5}$ mbar. A tungsten halogen lamp (Halonix, India) of 500W was used for illumination. The infrared (IR) part of the light was cut off using IR filters. The intensity of light was measured using a digital lux meter (LX–101, Lutron, Taiwan). The intensity of the light was varied by changing distance between the sample and halogen lamp and not by changing the current through halogen lamp. This was done so as to ensure the homogeneity in the relative contribution of spectral wavelengths in incident light. The photocurrent is calculated by subtracting the dark current from the total current measured in presence of light. The current was measured using a digital picoammeter (DPM–111 Scientific Equipments, Roorkee). During photoconductivity studies the electrodes were well-covered using aluminum foil to avoid photo diffusion. For the electrical studies, a special type of sample holder was used. The schematic diagram of the sample holder is shown in Figure 3.2. It consists of a copper base, on which thin film sample was mounted. A PT–100 thermocouple was placed very near to the sample to record the temperature of the sample. A micro-heater was attached to the copper base plate to vary the temperature of
the sample. Liquid nitrogen was used as coolant for low temperature conductivity measurements. The dark conductivity ($\sigma_d$) of the films was calculated by using following relation:

$$\sigma_d = \frac{I \times \rho}{A \times V} \text{Ω cm}^{-1} \quad (3.3)$$

Where $l$ is electrode gap, $A$ is the area of cross section and is given as $A = d \times w$, $d$ is thickness and $w$ is the width of the thin film respectively, $I$ is the current flowing through the sample and $V$ is the voltage applied to the electrode of the samples. However, the dc conductivity measurements for thin films of thickness ~76 to 81nm were carried out in the temperature range 288–358K in a running vacuum of $10^{-5}$ mbar.

### 3.8 Annealing Studies

Annealing studies were performed for both bulk as well as thin film samples. The detail of the annealing studies performed on bulk samples is as follows: small portion of as-prepared bulk samples of each composition was vacuum sealed in cleaned quartz ampoule under vacuum of ~$10^{-5}$ mbar. The cleaning and sealing of the quartz ampoule is done in the same way as described earlier in the section “Preparation of Bulk Samples”. The vacuum sealed ampoule of each composition was annealed inside the furnace at 348K and 398K for 12h. After annealing, the ampoule were allowed to slowly cool down and afterward samples were extracted from each of the ampoule and structural analysis was performed with the help of XRD to study the evolution of different crystalline phases emerged in different compositions. The thermal annealing of thin films was carried out in the bell jar of the vacuum system in the running vacuum of $10^{-5}$ mbar with heater fitted inside. The digital temperature controller with a power supply was used to control the temperature at the sample. The thin films grown by thermal evaporation method were annealed in high vacuum of the order $10^{-5}$ mbar. Thin films of thickness ~943 to 962nm were annealed 15K above their glass transition temperature. The ultra-thin films of thickness ~76 to 81nm were annealed at 328K (below $T_g$) and 343K (in between $T_g$ and $T_c$). The crystalline phases are identified with the help of JCPDS database (1998). Electrical and optical studies were carried out on annealed ultra-thin films.