Chapter 2

Experimental Techniques

2.1 Introduction

Amorphous materials are prepared through non-equilibrium processes. The physical properties of these materials therefore greatly depend on how samples are prepared. The preparation methods used at present can be classified, in principle, into the following two categories: (1) quenching from the liquid state (melt) and (2) condensation from the gas phase. There are of course other methods, for example, irradiation by ionizing particles (ion bombardment), sol-gel process, etc. Ion bombardment of c-solids produces structural damage and amorphizes the material, in particular surface layers, and is of great technological importance in the current crystalline Si industry. Through implanting the dopant atoms (e.g. P or B) the electronic properties are controlled. Amorphization with implantation is removed easily by laser annealing. The technique of the sol–gel method has great technological advantages in silica glass. Material for present study is prepared by quenching from melt technique.

A liquid may be solidify in two ways:

1) Discontinuously to a crystalline solids
2) Continuously to an amorphous solids (glass)

Two solids resulting from these two quite different ways follow different paths in Fig. 2.1. Crystalline solids are formed when supercooled liquid follow path (ABCF), while a glassy material is obtained along path (ADE) in volume versus temperature curve V(T). Some materials do not crystallize below their melting temperature and they become a supercooled liquid. A schematic illustration in Fig. 2.1 shows the volume versus temperature curve in glassy (amorphous), crystalline and liquid states. The liquid → glass transition is marked by discontinuity in V(T), an abrupt contraction to the volume of the crystalline solids. In a quenching experiment carried out at a sufficiently low cooling rate, route (ABCF) taken to arrive at the solid state. But at sufficiently high cooling rates, it is found that most materials alter their
behavior and follow the route (ADE) to the solid phase. $T_m$ (or $T_t$) is bypassed without incident, and the liquid phase persists until a lower temperature $T_g$ is reached, the materials undergo the so-called glass transition, which occurs at a certain temperature, $T_g$, below which they become glasses.

Most chalcogenide and oxide glasses can be prepared by the melt quenching (MQ) method. It is of interest to note that $T_g \approx \frac{2T_m}{3}$ is empirically obtained for most glasses, where $T_m$ is the melting temperature [1]. Factors that determine the glass-transition temperature are still not known, while the correlation between $T_g$ and the average coordination number $Z$ has been found to obey [2]

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

Fig. 2.1 Schematic illustration of the volume versus temperature curve. $T_g$ and $T_m$ denotes the glass transition and melting temperatures, respectively.

Amorphous materials produced by the MQ technique are usually called glasses. The term, glasses, may have some historical reasons, since so-called glasses are obtained from the MQ technique.
2.2 Material preparations

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 1 mm 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.

Table 2.1 The stoichiometric weight of the various constituents of sample a-(Ge$_{0.20}$Se$_{0.80}$)$_{0.90}$M$_{0.10}$ (M = Ag, Bi, Pb).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Element</th>
<th>Stoich.</th>
<th>Atomic weight (a.m.u)</th>
<th>Atomic weight × percentage</th>
<th>Actual weight taken for making (5g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ge$<em>{0.20}$Se$</em>{0.80}$)$<em>{0.90}$Ag$</em>{0.10}$</td>
<td>Ge</td>
<td>0.180</td>
<td>72.59</td>
<td>13.0662</td>
<td>0.8096</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>0.720</td>
<td>78.96</td>
<td>56.8512</td>
<td>3.5222</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>0.100</td>
<td>107.86</td>
<td>10.7860</td>
<td>0.6682</td>
</tr>
<tr>
<td>(Ge$<em>{0.20}$Se$</em>{0.80}$)$<em>{0.90}$Bi$</em>{0.10}$</td>
<td>Ge</td>
<td>0.180</td>
<td>72.59</td>
<td>13.0662</td>
<td>0.7194</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>0.720</td>
<td>78.96</td>
<td>56.8512</td>
<td>3.1300</td>
</tr>
<tr>
<td></td>
<td>Bi</td>
<td>0.100</td>
<td>208.98</td>
<td>20.8980</td>
<td>1.1506</td>
</tr>
<tr>
<td>(Ge$<em>{0.20}$Se$</em>{0.80}$)$<em>{0.90}$Pb$</em>{0.10}$</td>
<td>Ge</td>
<td>0.180</td>
<td>72.59</td>
<td>13.0662</td>
<td>0.7208</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>0.720</td>
<td>78.96</td>
<td>56.8512</td>
<td>3.1362</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>0.100</td>
<td>207.20</td>
<td>20.7200</td>
<td>1.1430</td>
</tr>
</tbody>
</table>

Materials are prepared by taking constituent elements of purity 99.999 % in required atomic weight percentages (see table 2.1). The electronic balance used for these measurements has an accuracy of 0.0001gm. Table 2.1 represents the method used to calculate the stoichiometric weight of the various constituents of samples a-
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 ice water. The glassy materials in the form of ingots were obtained by breaking the quartz tubes.

2.3 Thin films Preparations

The methods by which thin films can be prepared are broadly classified in two categories: physical methods and chemical methods of depositions. Physical methods for thin film deposition are vacuum evaporation, electron-beam evaporation, RF sputtering, ion beam evaporation. Some of the chemical methods for thin film deposition are chemical bath deposition, chemical vapor deposition, cathode electrolytic deposition, 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: 1 cm x 1cm). The conductivity of the glass (substrate) is very low ($\approx 10^{-14}$ $\Omega^{-1}cm^{-1}$). Cleaning of the substrate used in thin film deposition is very important because 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 (\(-2 \times 10^{-5}\) 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.

![Schematic diagram of the thin film coating unit used to deposit the thin films](image-url)

*Fig. 2.2 Schematic diagram of the thin film coating unit used to deposit the thin films*
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 they are used for irradiation experiment attain thermodynamic equilibrium. Schematic diagram of the thin film coating unit is shown in Fig. 2.2. Thickness of the sample is calculated using transmission method. The deposition parameters are kept identical for all alloys to make comparison of their properties.

2.4 SHI irradiation

2.4.1 Working principle of Pelletron accelerator

Swift heavy ion irradiation in the current work have been done at “15 UD Pelletron accelerator” available at the ‘Inter University Accelerator Centre (IUAC)’, New Delhi, India. The model 15 UD Pelletron is a tandem electrostatic accelerator capable of almost delivering any ion form periodic table upto the energy of 200 MeV depending on ion. This electrostatic accelerator at IUAC is installed with a vertical configuration in an insulating tank which is 26.5 meters in length and 5.5 meters in diameter and filled with SF6 as an insulating gas. This accelerator is capable of generating terminal voltage up to 15 million volts and ions of the required elements with energy of few hundred million electron volts (MeV). This terminal voltage can be varied from 4 to 15 MV. This variable voltage terminal is connected to the tank vertically through ceramic titanium tubes called accelerating tubes. A potential gradient is maintained through these tubes from high voltage to ground from the top of the tank to the terminal as well as from the terminal to the bottom of the tank.

Fig. 2.3 shows schematic of the 15 UD Pelletron accelerator. Negative ions are generated in the SNICS (source of negative ions by cesium sputtering) ion source. The sputter source uses accelerated cesium ions, striking a cold cathode, to produce a negative ion beam of cathode material. A thin layer of cesium condensed over the cathode surface enhances negative ion production. These ions are extracted from the ion source by applying a positive injection voltage (generally \(V_{inj}=220\text{ kV}\)), with an energy \(E_{inj} = q V_{inj}\) where \(q\) is the charge state of the ion \((q=1)\). These singly charged ions are then mass analysed (by injector magnet) and are accelerated towards the Pelletron accelerator which is set with a positive terminal voltage of \(V\). It will then
acquire an energy, $E_1 = V$, (since $q=1$). Now the ‘Charge stripper’ stripes off the electrons from the ions to make the ions multiply charged positive ions.

**Fig. 2.3 Schematic representation of working principle of 15 UD pelletron**

These positive ions are again accelerated with positive potential $V$ so that the energy becomes, $E_2 = qV$, (where $q$ is the charge state of the multiply charged ion). The terminal also has an offset quadruple triple lens with variable aperture and Faraday cup to select the desired charge state after stripping of electrons from the ions. In the terminal the negative ions are stripped off few electrons and thereby converted to positive ions, which are further accelerated as they proceed to the bottom of the tank at ground potential. As a result the ions emerging out of the accelerator gain energy given by $E = E_{inj} + (q+1)V$ MeV. These high energy ions are then analyzed to the required energy with the help of a $90^\circ$ bending magnet known as analyser magnet, and directed to the desired experimental area with the help of multiport switching magnet.
which can deflect the beam into any of the beam lines in the beam hall [3]. The irradiation of samples has been performed in the material science beam line (Fig. 2.4).

2.4.2 Irradiation fluence estimation

The beam fluence was estimated by using the formula

$$I = \frac{Q}{T} = \frac{qeD}{T} = \frac{qe\phi A}{T}$$

$$\phi = \frac{IT}{qeA}$$

where, $T$ = time of irradiation (measured in seconds)
$q$ = charged state of ion
$e = 1.6 \times 10^{-19} \text{C}$
$I$ = ion current (nA)
$Q$ = total charge
$D = \phi A = \text{ion fluence per cm}^2 \times \text{area (A) in cm}^2$
Since, number of particles per nano amperes of the beam current is given by

\[ \frac{I}{qe} (pnA) \]

Therefore,

\[ \phi = T \times \text{beam current (pnA)} \]

\[ \frac{A}{T} \]

By using this formula, irradiation fluence required for all irradiation time was calculated. By keeping beam current constant, the samples were irradiated for a different irradiation fluence.

2.4.3 Calculations of electronic and nuclear loss by SRIM code

SRIM-code is a group of programs which calculate the stopping and range of ions into a matter using a quantum mechanical treatment of ion-atom collisions. This calculation is made very efficient by the use of statistical algorithms which allows the ions to make jumps between the calculated collisions and then averaging the collision results over the intervening gap. During the collisions, the ion and the atom have a screened Coulomb collision, including the exchange and correlation interactions between the overlapping electron shells. The ions have long range interactions creating excitations within the target. These are explained by including a description of the target’s collective electronic structure and interatomic bond structure. The charged state of the ion within the target is described by using the concept of effective charge, which includes a velocity dependent charge state and long range screening due to the collective electron sea of the target. The particle’s energy reduced after each free flight path by the amount of electronic energy loss and then (after the collision) by the transferring the momentum to target atom by collision, which is termed as nuclear energy loss (dE/dx)_n. So, by using SRIM code we can calculate the ion destruction and for quick calculation of damage, details regarding full damage cascades and surface sputtering calculations etc.

2.4.4 Irradiation Using 15 UD Pelletron

The samples were irradiated with both silver ions and oxygen ions beam with varying fluence using 15 UD Pelletron Accelerator, at Inter University Accelerator (IUAC), New Delhi. In present work we have calculated (see table 2.2) the electronic energy loss, nuclear energy loss and projected range of 100 MeV silver ions and 85
MeV oxygen ions in \( a-(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}\text{M}_{0.10} \) (\( M = \text{Ag, Bi, Pb} \)) samples using SRIM 2008 Code [5].

**Table 2.2 Irradiation details of irradiated samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ion beam and energy</th>
<th>Fluence range (ions/cm(^2))</th>
<th>Electronic energy loss (keV/A(^0))</th>
<th>Nuclear energy loss (eV/A(^0)) &amp; (Range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ge}<em>{0.20}\text{Se}</em>{0.80})<em>{0.90}\text{Ag}</em>{0.10} )</td>
<td>100 MeV Ag beam</td>
<td>( 1 \times 10^{11} -3 \times 10^{13} )</td>
<td>1.53 keV/A(^0)</td>
<td>9.99 eV/A(^0) 12.12 ( \mu )m</td>
</tr>
<tr>
<td></td>
<td>85 MeV O beam</td>
<td>( 1 \times 10^{12} -1 \times 10^{14} )</td>
<td>0.12 keV/A(^0)</td>
<td>0.08 eV/A(^0) 51.02 ( \mu )m</td>
</tr>
<tr>
<td>( \text{Ge}<em>{0.20}\text{Se}</em>{0.80})<em>{0.90}\text{Bi}</em>{0.10} )</td>
<td>100 MeV Ag beam</td>
<td>( 1 \times 10^{11} -3 \times 10^{13} )</td>
<td>1.39 keV/A(^0)</td>
<td>9.33 eV/A(^0) 13.1 ( \mu )m</td>
</tr>
<tr>
<td></td>
<td>85 MeV O beam</td>
<td>( 1 \times 10^{12} -1 \times 10^{14} )</td>
<td>0.11 keV/A(^0)</td>
<td>0.07 eV/A(^0) 55.58 ( \mu )m</td>
</tr>
<tr>
<td>( \text{Ge}<em>{0.20}\text{Se}</em>{0.80})<em>{0.90}\text{Pb}</em>{0.10} )</td>
<td>100 MeV Ag beam</td>
<td>( 1 \times 10^{11} -3 \times 10^{13} )</td>
<td>1.43 keV/A(^0)</td>
<td>9.59 eV/A(^0) 12.92 ( \mu )m</td>
</tr>
<tr>
<td></td>
<td>85 MeV O beam</td>
<td>( 1 \times 10^{12} -1 \times 10^{14} )</td>
<td>0.13 keV/A(^0)</td>
<td>0.07 eV/A(^0) 53.91 ( \mu )m</td>
</tr>
</tbody>
</table>

The projected range of 100 MeV Ag beam in \( \text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}\text{Ag}_{0.10} \) thin film samples calculated by SRIM is 12.12 \( \mu \)m. The electronic energy loss \((\text{dE/}dx)_{e}\) and nuclear energy loss \((\text{dE/}dx)_{n}\) of the ions in \( \text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}\text{Ag}_{0.10} \) thin film samples are 1.53 KeV/A\(^0\) and 9.99 eV/A\(^0\) respectively. The projected range 85 MeV oxygen ions in \( \text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}\text{Ag}_{0.10} \) thin film samples is 51.02 \( \mu \)m. The electronic energy loss
(dE/dx)_c and nuclear energy loss (dE/dx)_n in (Ge_{0.20}Se_{0.80}O_{0.90}Ag_{0.10} thin film samples are 0.12 keV/A° and is 0.08 eV/A° respectively. The projected range of 100 MeV Ag ions in (Ge_{0.20}Se_{0.80}O_{0.90}Ag_{0.10} thin film samples calculated by SRIM is 13.1 μm. The electronic energy loss (dE/dx)_c and nuclear energy loss (dE/dx)_n in (Ge_{0.20}Se_{0.80}O_{0.90}Ag_{0.10} thin film samples are 1.39 keV/A° and 9.33 eV/A° respectively. The projected range 85 MeV oxygen ions in (Ge_{0.20}Se_{0.80}O_{0.90}Ag_{0.10} thin film samples is 55.58 μm. The electronic energy loss (dE/dx)_c and nuclear energy loss (dE/dx)_n in (Ge_{0.20}Se_{0.80}O_{0.90}Ag_{0.10} thin film samples are 0.11 keV/A° and is 0.07 eV/A° respectively.

The projected range of 100 MeV Ag beam in (Ge_{0.20}Se_{0.80}O_{0.90}Pb_{0.10} thin film samples calculated by SRIM is 12.92 μm. The electronic energy loss (dE/dx)_c and nuclear energy loss (dE/dx)_n in (Ge_{0.20}Se_{0.80}O_{0.90}Pb_{0.10} thin film samples are 1.43 keV/A° and 9.59 eV/A° respectively. The projected range 85 MeV oxygen ions in (Ge_{0.20}Se_{0.80}O_{0.90}Pb_{0.10} thin film samples is 53.91 μm. The electronic energy loss (dE/dx)_c and nuclear energy loss (dE/dx)_n in (Ge_{0.20}Se_{0.80}O_{0.90}Pb_{0.10} thin film samples are 0.13 keV/A° and is 0.07 eV/A° respectively.

It is clear from the table 2.2 that in all irradiated samples due to the large stopping range of the ions, which is greater than the thickness of the our thin film samples, which is approximately 450 nm, ions passes the thin films and come to rest in glass substrate.

2.5 Characterization technique

The pristine and irradiated samples were analyzed with different characterization techniques to study change in their optical, electrical, structural and surface morphology. Different characterization techniques and working principles of some of them have been discussed in the following subsections.

2.5.1 X-Ray diffraction

X-rays are electromagnetic radiation with wavelength of the order of 1 Å, which is about the same size as that of atom. The role of X-rays in the material science is to characterize the nature of the materials whether it is crystalline or amorphous in nature. Each crystalline sample has its unique X-ray pattern which may
change when we give different treatments to the materials under investigation. X-ray is one of most important tools in the material science. The amorphous nature of thin films before and after irradiation was confirmed by using X-ray diffraction technique for all the samples. Absence of any prominent peak in all the samples both before and after irradiation and thin film form confirms the amorphous nature of the samples. All XRD measurements were performed at IUAC, New Delhi.

2.5.2 UV-Visible spectroscopy

The UV-Visible spectroscopy is a measurement of the attenuation of light beam after it passes through the material under investigation. We have performed the transmission measurements on all pristine and irradiated samples in order to calculate the different optical parameters. The transmission spectrum is obtained from visible-near Infrared (VIS/NIR) computer-controlled spectrophotometer [SOLAR-TII MS 2004].

![Schematic layout monochromator-spectrograph (SOLAR TII, MS 2004)](image)

*Fig. 2.5 Schematic layout monochromator-spectrograph [SOLAR TII, MS 2004] used to measure the transmission spectra.*
The range for the transmission spectrum is taken from 400 nm to 1700 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. 2.5. 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.

2.5.3 Atomic Force Microscopy (AFM)

Scanning probe microscopes (SPM) define a broad group of instruments used to image and measure properties of material, chemical, and biological surfaces. SPM images are obtained by scanning a sharp probe across a surface while monitoring and
compiling the tip-sample interactions to provide an image. The two primary forms of SPM are scanning tunneling microscopy (STM) and atomic force microscopy (AFM). STM was first developed in 1982 at IBM in Zurich by Binnig, et al. [6]. The invention of the scanning tunneling microscope (for which Binnig and Rohrer were awarded the Nobel Prize in Physics in 1986) has had a great impact on the technical community by providing a new and unique tool to advance fundamental science and technology. Although the ability of the STM to image and measure material surface morphology with atomic resolution has been well documented, only good electrical conductors are candidates for this technique. This significantly limits the materials that can be studied using STM and led to the development, in 1986, of the atomic force microscope by (AFM) [7]. This enabled the detection of atomic scale features on a wide range of insulating surfaces that include ceramic materials, biological samples, and polymers.

The principal behind the operation of an AFM in the contact mode is shown in Figure 2.6. The AFM tip is first brought (manually) close to the sample surface, and then the scanner makes a final adjustment in tip-sample distance based on a setpoint determined by the user. The tip, now in contact with the sample surface through any adsorbed gas layer, is then scanned across the sample under the action of a piezoelectric actuator, either by moving the sample or the tip relative to the other. A laser beam aimed at the back of the cantilever-tip assembly reflects off the cantilever surface to a split photodiode, which detects the small cantilever deflections. A feedback loop, shown schematically in Fig.2.6, maintains constant tip-sample separation by moving the scanner in the z direction to maintain the setpoint deflection. Without this feedback loop, the tip would “crash” into a sample with even small topographic features (although this phenomenon can happen even with careful AFM operation). By maintaining a constant tip-sample separation and using Hooke’s Law ($F = -kx$ where $F$ is force, $k$ is the spring constant, and $x$ is the cantilever deflection), the force between the tip and the sample is calculated. The distance the scanner moves in the z direction is stored in the computer relative to spatial variation in the $x$-$y$ plane to generate the topographic image of the sample surface.

The AFM tips are usually micro-fabricated silicon cones or silica nitride four sided pyramids that are commercially available mounted to the cantilevers with spring of 0.05-1.5 N/m for contact mode and 40-80 N/m for tapping mode. These tips are not
solids but are hollow, which improves their performance. For present study, the surface morphological studies were done using a Multimode IIIa, Digital Instruments atomic force microscope at IUAC, New Delhi. AFM provides valuable information regarding the surface roughness of both pristine and irradiated chalcogenide thin film samples.

![AFM facility in the new LEIB (Low energy ion beam) building at IUAC, New Delhi (left) [8] and schematic diagram of AFM (right) [9]](image)

**Fig. 2.6** The AFM facility in the new LEIB (Low energy ion beam) building at IUAC, New Delhi (left) [8] and schematic diagram of AFM (right) [9]

### 2.6 Raman Spectroscopy

Since the first reports of its experimental discovery in the late 1920s [10, 11], Raman spectroscopy has gone through several stages of development. For many years, however, it remained something of an esoteric technique, based on the inelastic scattering of light, in which the filtered mercury arc excitation sources used in the early stages of its development necessitated accumulation over very lengthy exposure times to achieve acceptable signal levels. In the 80 years since its discovery and announcement, the Raman Effect has experienced two periods of growth and widening of interest: (i) in the 1960s with the advent of the laser as an intense monochromatic light source; (ii) in the 1980s with advances in detector, filter and diode laser technology (Fig. 2.8) [12, 13]. Indeed. It is probably within the last two decades that the phenomenon of Raman scattering has seen its most rapid growth and popularity both in terms of the range of application to scientific problems and in the development of a number of techniques with Raman as a central feature for probing
molecular structure, both in ground and electronically excited states. When monochromatic light impinges on a sample, much of it passes through the sample unchanged or some may be absorbed, depending upon the wavelength of the light and the nature of the sample. A small fraction, some 0.1%, is elastically scattered, as light of the same frequency as the incident light (Rayleigh scattering). An even smaller fraction of the incident light, perhaps amounting to 1 photon in $10^5$ or $10^7$, will be scattered inelastically (Raman scattering), either towards lower frequencies (Stokes scattering) or higher frequencies (anti-Stokes scattering), than the incident light.

2.6.1 Theoretical basis of Raman Effect

The scattering of light may be thought of as the redirection of light that takes place when an electromagnetic (EM) wave (i.e. an incident light ray) encounters an obstacle or nonhomogeneity, in our case the scattering material (solid, liquid or gas). As the EM wave interacts with the matter, the electron orbits within the constituent molecules are perturbed periodically with the same frequency ($\nu_0$) as the electric field of the incident wave. The oscillation or perturbation of the electron cloud results in a periodic separation of charge within the molecules, which is called an induced dipole moment. The oscillating induced dipole moment is manifest as a source of EM radiation, thereby resulting in scattered light. The majority of light scattered is emitted at the identical frequency ($\nu_0$) of the incident light, a process referred to as elastic scattering. However, as explained below, additional light is scattered at different frequencies, a process referred to as inelastic scattering. Raman scattering is one such example of inelastic scattering. In summary, the above comments describe the process of light scattering as a complex interaction between the incident EM wave and the material’s molecular/atomic structure.

As discussed above, an incident electromagnetic wave induces a dipole moment during the light material interaction. The strength of the induced dipole moment, $P$, is given by

$$P = \alpha E$$  \hspace{1cm} (1.1)

where $\alpha$ is the polarizability and $E$ is the strength of electric field of the incident EM wave. The polarizability is a material property that depends on the molecular structure and nature of the bonds. For the incident EM wave, the electric field may be expressed as
\[ E = E_0 \cos(2\pi v_0 t) \]  
(1.2)

where \( v_0 \) is the frequency (Hz) of the incident EM (\( v_0 = \frac{c}{\lambda} \)). Substituting eq. (1.2) into (1.1) yields the time-dependent induced dipole moment,

\[ P = \alpha E_0 \cos(2\pi v_0 t) \]  
(1.3)

Because the ability to perturb the local electron cloud of a molecular structure depends on the relative location of the individual atoms, it follows that the polarizability is a function of the instantaneous position of constituent atoms. For any molecular bond, the individual atoms are confined to specific vibrational modes, in which the vibrational energy levels are quantized in a manner similar to electronic energies. The vibrational energy of a particular mode is given by

\[ E_{vih} = \left( j + \frac{1}{2} \right) h v_{vih} \]  
(1.4)

where \( j \) is the vibrational quantum number (\( j = 0, 1, 2, \ldots \)), \( v_{vih} \) is the frequency of the vibrational mode, and \( h \) is the Planck constant.

The physical displacement \( dQ \) of the atoms about their equilibrium position due to the particular vibrational mode may be expressed as

\[ dQ = Q_o \cos(2\pi v_0 t) \]  
(1.5)

where \( Q_o \) is the maximum displacement about the equilibrium position. For a typical diatomic molecule (e.g. \( N_2 \)), the maximum displacement is about 10% of the bond length. For such small displacements, the polarizability may be approximated by a Taylor series expansion, namely,

\[ \alpha = \alpha_o + \frac{\partial \alpha}{\partial Q} dQ \]  
(1.6)

where \( \alpha_o \) is the polarizability of the molecular mode at equilibrium position. Based on the vibrational displacement of Eq. (1.5), the polarizability may be given as

\[ \alpha = \alpha_o + \frac{\partial \alpha}{\partial Q} Q_o \cos(2\pi v_0 t) \]  
(1.7)

Finally, Eq. (1.7) may be substituted into Eq. (1.3), which yields

\[ P = \alpha_o E_0 \cos(2\pi v_0 t) + \frac{\partial \alpha}{\partial Q} Q_o E_0 \cos(2\pi v_0 t) \cos(2\pi v_0 t) \]  
(1.8)

Using a trigonometric identity, the above relation may be recast as
\[ P = \alpha_0 E_0 \cos(2\pi v_t) + \left( \frac{\partial \alpha E_0}{\partial Q} \right) \cos \left\{ 2\pi (v_0 - v_{\text{ vib}}) t \right\} + \cos \left\{ 2\pi (v_0 + v_{\text{ vib}}) t \right\} \] (1.9)

Examination of the above equation reveals that induced dipole moments are created at three distinct frequencies, namely \( v_0, \) \( (v_0 - v_{\text{ vib}}), \) and \( (v_0 + v_{\text{ vib}}), \) which results in scattered radiation at these same three frequencies [14-16]. The first scattered frequency corresponds to the incident frequency, hence is elastic scattering (Rayleigh), while the latter two frequencies are shifted to lower or higher frequencies and are therefore inelastic processes. The scattered light in these latter two cases is referred to as Raman scattering, with the down-shifted frequency (longer wavelength) referred to as Stokes scattering, and the up-shifted frequency (shorter wavelength) referred to as anti-Stokes scattering. C.V. Raman was the first to describe this type of inelastic scattering, for which he was awarded the Noble prize in physics in 1930.

2.6.2 Raman Microscope at IUAC

We have performed all our measurements of pristine and irradiated samples using InVia Raman microscope from Renishaw UK, installed at IUAC, New Delhi. The system consists of Ar ion laser with 514.5 nm wavelength and 50 mw power. The Microscope is shown in fig 2.7. The microscope has very high sensitivity integrated components which enables high resolution confocal measurements.

![Fig. 2.7 Renishaw InVia Raman Microscope at IUAC, New Delhi](image)

Setup can also support multiple lasers, with automatic software switching of excitation wavelength. Exceptional sensitivity for ultra-low signal detection with
minimum noise is possible with compact RenCam charge coupled detector (CCD) (105 mm x 105 mm x 135 mm). It is thermoelectrically cooled and operates at -70 °C without the need for additional cryogenic coolants and it is deep depletion with UV enhanced coating for future UV excitation applications. The detector is sensitive from 100 to 3200 cm\(^{-1}\). The lower limit is set by the notch filter used for suppressing the Raleigh background of laser.

2.6.3 Working Principle and schematic diagram

The basic schematic of the optics in the Rainshaw Raman Microscope is shown in figure 2.8. Light from the 514.5 nm laser is reflected by a holographic 514.5 nm line reject filter into a sample under investigation via a microscope objective.

Fig. 2.8 Schematic representation of micro-Raman setup

Light is then reflected from the sample back into the line reject filters which allow Stokes and anti-Stokes shifted light into the spectrometer but rejects the Rayleigh scattered light. The spectrometer consists of a diffraction grating and CCD camera which allows the continuous and static scan to be taken.
2.7 Electrical 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

\[ \sigma_{dc} = \sigma_0 \exp(-\Delta E / kT) \]

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. 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:

\[ \sigma = L / RA \]

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

\[ A = bt \]

where, \( b \) is length and \( t \) is the thickness of the thin film.

To carry out the various electrical measurements on the thin films (dc and photocconductivity measurements) at different temperatures, a specially designed metallic sample holder, as shown in figure 2.9, is fabricated in the laboratory. Stainless steel is used for making the sample holder to take care of surface currents and unwanted disturbances in the measurements of small currents (pA). It also helps to provide proper shielding to the thin film samples for the accurate current measurements during various experimental observations. At low and high temperature, stainless steel is highly durable and corrosion free. The sample holder is fitted with a Chromel-Alumel thermocouple through teflon tape. The junction of the thermocouple is placed on copper block very near to thin film so that the chance of error in the temperature measurement of thin film is less. A small circular glass window is installed in the sample holder directly above the space at which film is
placed on the copper block. This copper block is connected to the base of the sample holder through a copper rod. By this arrangement, the temperature gradient is very small between the copper block and base of the sample holder.

The light could be shone through the glass window to carry out the photoconductivity measurements on thin films. To cut off the IR part of the light, water in transparent petri dish is kept above the glass window while taking the various photoconductivity measurements. The Cu block from lower side is fitted with heater to anneal the films and to study their behavior with rise in temperature. These heaters are connected to a variac through Teflon feed from outside the sample holder to vary the rate of heating. The rate is monitored through the display of the digital panel meter which is connected to the thermocouple. The current is measured by a digital pico-ammeter (DPM-111) with an accuracy of 1pA. The sample holder is connected to rotary vacuum pump to maintain a vacuum ~ $10^{-3}$ mbar throughout the measurements.
References


[8] IUAC, New Delhi, Annual Report, p-100


