3 Experimental Techniques

In this chapter experimental techniques and experimental set-ups (on-line and off-line) are described in detail into four sections: (i) ERDA technique, (ii) on-line experiments (iii) catcher technique for sputtering yield measurements of thick target, (iv) off-line experiments for characterization of the samples

3.1 ERDA technique

MeV ion-beam analysis with light ions has been demonstrated to be a powerful technique for sensitive measurements of depth profiles of light elements in solids. Particularly, Rutherford back-scattering (RBS) with low energy $^4$He ions has been extensively used in materials studies. Major difficulties, however, arise in this method, essentially for light elements, due to (i) poor sensitivity of light elements, (ii) overlapping of scattered ion energies for light elements and (iii) H depth profiling was not possible, as He cannot get scattered back from H.
L’Ecuyer et al. [1] proposed the ERDA technique to determine the concentration of light elements in heavy substrates, by using $^{35}$Cl ions of 30 MeV and absorbers before the detector in order to discriminate between scattered heavy ions and recoiling atoms. Most common application of ERDA after its discovery has been the hydrogen depth profiling in various materials [2]. In the beginning, this technique developed rather slowly [2-5]. Later with development of heavy ion accelerators and efficient detection systems, a significant progress took place [6,7]. Recently the potentials of ERDA as a standard technique for the on-line study of swift heavy ion induced modifications of materials have been demonstrated [8,9]. In this section, the principles of ERDA will be described, followed by a brief description of this technique with telescope detector. The construction of a large solid angle $\Delta E-E$ telescope detector at NSC and its performance will be highlighted.

### 3.1.1 Principles of ERDA

When an ion of mass $m_p$ strikes a target atom of mass $m_n$, scattering takes place. In the collision, the incident ion imparts some energy to the atom at rest and gets scattered at an angle $\theta$. The target atom gets recoiled at an angle $\varphi$. The recoil energy ($E_r$) of the atom depends on mass of the projectile ion, mass of the target atom, energy of the incident ion ($E_p$) and the recoil angle $\varphi$. Pictorial representation of the scattering process is depicted in figure 3.1.
Figure 3.1: Schematic of ion-atom scattering in ERDA

Mathematically, it is given by the following expression, which can be derived using the laws of conservation of energy and momentum:

\[ E_r = \frac{4m_p m_t \cos^2 \phi}{(m_p + m_t)^2} E_p \]  

(3.1)
Since the projectile mass $m_p$, its energy $E_p$ and recoil angle remains fixed under a given experimental condition, different atoms (having different masses) present in the sample will have different recoil energies as governed by equation (3.1). Thus from the recoil energy spectrum, the masses of the elements present in any sample can be determined. The energy of the recoils from various depths at which they originate depends on three factors: (i) rate of energy loss of incoming ions in the material, (ii) the rate of energy loss of the recoil atoms in the material prior to emergence from the sample and (iii) the energy loss of the recoil atoms in the stopper foil which is used to stop the unwanted scattered ions and recoils. Using the above arguments, the depth scale can be generated in the recoil energy spectrum.

The quantitative estimation of an element in the sample can be made by measuring the number of recoils, $A_r$ (integrated counts of a recoiling species), detected for a given number of incident ions, $N_p$. The number of atoms/cm$^2$ of an element is given by the following expression

$$N_i = \frac{A_r \sin \alpha}{N_p \left(\frac{d\sigma}{d\Omega}\right) \Omega}$$  \hspace{1cm} (3.2)

Where $\alpha$ is the tilt angle, $\Omega$ is the solid angle subtended by the detector and $(d\sigma/d\Omega)$ is the Rutherford recoil cross section given by,
where $Z_p$ and $Z_t$ are atomic numbers of projectile and target atoms respectively. The schematic of ERDA geometry is shown in figure 3.2.

Figure 3.2: Schematic representation of ERDA geometry
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Energy to depth scale conversion of the recoil spectrum is carried out using the following algorithm.

The energy of recoil from the surface is given by $E_s$ as expressed as

$$E_s = KE_p$$  \hfill (3.4)

Where $K$ is the kinematic factor given by

$$K = \frac{4m_p m_r E_p}{(m_p + m_r)^2}$$  \hfill (3.5)

From the schematic representation of figure 3.2, one can see that the recoils from the surface have the maximum energy. Thus, maximum recoil energy represents the surface. The energy of any recoil ($E_d$) originating from a depth $d$ is given by,

$$E_d = K \left[ E - \frac{d}{\sin \alpha} (dE/dx)_m \right]$$  \hfill (3.6)

where $(dE/dx)_m$ is the stopping power of a material for the incoming ion. The recoil energy after coming out of the surface originating at depth $d$ is,

$$E_{ds} = E_d - \frac{d}{\sin \phi \sin \alpha} (dE/dx)_{out}$$  \hfill (3.7)

where $(dE/dx)_{out}$ is the stopping power of material for the recoil. The energy of the recoil as detected by the detector is given by,
where, $\Delta E_{\text{foil}}(E_{ds})$ is the energy loss of the recoil ion in the stopper foil, which is a function of the recoil energy $E_{ds}$.

### 3.1.2 ERDA with telescope detector

For simultaneous detection of lower and higher masses present in any compound film, ERDA technique is equipped with detection systems capable of mass discrimination [6-9]. Telescope detector is one of such systems. The commercially available detector telescope consists of transmission type thin solid state surface barrier detector (SSBD) to measure $\Delta E$ (a small part of the energy) and a thick solid state detector for the remaining energy, $E_{\text{rest}}$ [10]. This simple commercial particle identification system has serious limitation in its use for heavier recoil detection due to radiation damage. If the telescope consists of a gas ionization chamber and SSBD, it offers several advantages. There is no radiation damage in ionization chamber, the detector thickness is homogeneous and can be adjusted to the requirements of a certain measurement just by changing the gas pressure. It can be indigenously built as per requirement. Though there will be radiation damage in the SSBD, but this can be taken care of by making special design of ionization chamber to work as a telescope for almost all the masses except very low mass element (H, He etc). The SSBD can be used only as a stop detector for low masses.
(H to O). Therefore, the radiation damage is minimized. This combination is a simple, but very effective detection system for heavy ion ERDA [7].

The basic physical process of identifying any element in the detector telescope is the energy loss. The energy loss is given by Bethe Bloch formula as follows [11]:

\[ -\frac{dE}{dx} = 4\pi n \left( e^4 / m \right) q_{eff} \left( \frac{e^2}{v^2} \right) \ln \left[ 2mv^2 / I(1 - \beta^2) - \beta^2 - S - D \right] \]  

(3.9)

where \( n \) is the number of electrons/cm\(^3\), \( e \) and \( m \) are the charge and mass of the electron, \( q_{eff} \) is the rms charge of the ion (in units of electronic charge), \( v \) is the ion velocity, \( \beta = v/c \), where \( c \) is the velocity of light, \( I \) is the mean ionization potential of the gas, \( S \) is the shell correction factor and \( D \) is the density correction factor. For light ions \( q_{eff} = Z \), the atomic number of the ion, but in case of heavy ions \( q_{eff} < Z \).

For fully stripped ions and neglecting the shell and density corrections an approximation of the equation (3.9) is,

\[ -\frac{dE}{dx} = AZ^2 \left( e^2 / v^2 \right) \ln \left[ Bv^2 / (e^2 - v^2) \right] \]  

(3.10)

where \( A \) and \( B \) are constants that depend only on detector material. For non-relativistic particles, \( v^2 = 2E/M \) and since the logarithmic term varies slowly with energy, a further simplified equation results:

\[ \frac{dE}{dx} = \frac{MZ^2}{E} \]  

(3.11)
This equation suggests that the product $E.dE/dx$ provides a measure of $MZ^2$. The algorithm, based on which the particle identification is carried out in telescope is:

The signals from $\Delta E$ and $E$ are added to give total energy ($E_{\text{tot}} = \Delta E + E_{\text{rest}}$). Different elements are separated in $\Delta E$ versus $E_{\text{tot}}$ plot according to their mass, governed by the following equation:

$$\frac{\Delta E}{\Delta x} \propto \frac{MZ^2}{(E_{\text{rest}} + \Delta E)} \quad (3.12)$$

in a typical 2 dimensional plot [6-8]. In equation (3.12), $\Delta x$ designates the thickness of the $\Delta E$ detector. For very heavy ions, i.e. $M_p \gg M_t$, recoil cross sections are nearly independent of recoil species as the cross section is proportional to $Z_t/M_t$ (from equation 3.3) which is almost a constant quantity [8]. Therefore, in the two dimensional plot, elemental separation of any thin film is possible.

The necessary parameter for such element separation study is the energy resolution of the set-up. The factors, which contribute to the energy resolution of the telescope detector system, are:

(i) The intrinsic detector resolution, $\delta E_d$, which is the quadratic sum of the (a) electronic noise (b) the $E$ detector and (c) $\Delta E$ detector resolution;

(ii) The geometrical broadening due to finite detector acceptance which causes kinematic broadening and designated as $\delta E_p$, it is given by the equation:

$$\delta E_p = -2K \sin \theta \cos \theta \quad (3.13)$$
(iii) The energy straggling, $\delta E_{\text{st}}$ in the target and the inhomogeneities and straggling in the telescope entrance foil;

(iv) The multiple scattering (i.e. the repeated elastic Coulomb scattering of ion and target nuclei) in the target and in the telescope entrance foil that causes angular and lateral spread and adds to the geometrical broadening, which can be designated as $\delta E_{\text{sc}}$.

The total energy resolution is then expressed as:

$$\delta E = \delta E_{d}^{2} + \delta E_{\beta}^{2} + \delta E_{\text{st}}^{2} + \delta E_{\text{sc}}^{2}$$  \hspace{1cm} (3.14)

One of the important factors to be taken care of in the ERDA, is the maximum angle ($\theta_{\text{max}}$) of scattered projectile, which is given by,

$$\theta_{\text{max}} = \sin^{-1} \frac{m_{t}}{m_{p}}$$  \hspace{1cm} (3.15)

In order to prevent excessive dead time and energy overlap due to the large elastic yield coming from the scattered beam, the recoil angle is chosen greater than $\theta_{\text{max}}$.

3.1.3 Development of large area $\Delta E$-$E$ telescope detector

To study electronic sputtering, it is necessary to make dynamic measurements in which the concentration analysis can be determined as a function of ion fluence [9]. A detector with a large solid angle is required for such measurements so that a sufficient number of recoils can be recorded for concentration analysis with reasonable statistics for small ion fluence. However, the use of a detector with large solid angle results in kinematic broadening, hampering the resolution. This can be
overcome if the detector is position sensitive so that the kinematic energy broadening can be corrected by software. This fact has motivated us to design and fabricate a large area position sensitive detector telescope (LAPSDT).

The set-up consists of a large solid angle (~4.8 msr) ΔE-E telescope detector with position sensitivity and is installed [12] at 45° port of the high vacuum chamber of the materials science beam line at NSC. In figure 3.3, a schematic of the materials science beam line is shown, where LAPSDT is installed.

Figure 3.3: Schematic of materials science beam line showing the LAPSDT
Before giving the details of the design and construction of the detector, let us see the purpose of large solid angle of this detector:

The necessary conditions for electronic sputtering study are (i) separation of nearby masses (e.g. C, N, O etc.), (ii) to use beam current as low as possible in order to avoid pulse pile up and to minimize the sample heating. Due to a very low beam current, the count rate reduces drastically. Larger solid angle of the detector can solve this problem. A comparative study of large (~6 msr) and small (~0.3 msr) solid angle detector is shown in the literature [9], which shows that it is almost impossible to make any quantitative estimation of ion induced modification by the detector having smaller solid angle due to poor statistics.

The schematic view of whole detector assembly starting from the 45^0 port of vacuum chamber is shown in figure 3.4.

Detector assembly can be divided into following parts: (i) detector housing, (ii) gas ionization chamber and electrodes, (iii) surface barrier detector, (iv) window and its support, (v) intermediate chamber and mask arrangement, and (vi) gas handling system. Each part of the detector is described below:

3.1.3.1 Detector housing

Detector housing is a cylindrical stainless steel chamber of length 31 cm and diameter 19 cm (inner), having thickness of 0.5 cm, where gas ionization chamber
(described in 3.1.3.2) and solid state surface barrier detector (described in 3.1.3.3) are housed.

Figure 3.4: Schematic diagram of telescope detector starting from outside of high vacuum chamber
At two opposite ends of the chamber two flanges are welded. Front flange has outer diameter or o. d. of 27 cm, inner diameter or i. d. of 8.9 cm and thickness, 1.5 cm. Back flange has 27 cm o.d, 19 cm i.d, and 1.5 cm thickness. The front flange is connected to the intermediate chamber (described in 3.1.3.5). At the back flange, over the O-ring a plate with two handles is fitted with the help of a supporting flange. All the electrical connections (LEMO feedthrough connection) are taken through backside of this plate. At the front side of the backplate (inside the detector house as in figure 3.4) the solid state detector is mounted. Four ports (three of size KF16 and one of KF25) are welded to the chamber. Three of these (KF16) are used as gas inlet, outlet and bypass (described in 3.1.3.6). The fourth one (KF25) is made for viewing the detector inside. Presently it is blanked off.

3.1.3.2 Gas ionization chamber and electrodes

Gas ionization chamber covers the major part of the detector housing, the detector medium being gas, the effective thickness of the active medium can be changed according to the requirement by changing the gas pressure. The basic building block of ionization chamber is the electrodes; anode, cathode and grid. Anode is a Ni cladded glass epoxy plate of 26.5 cm long and 9.5 cm wide, divided into two parts of length, 7.5 cm (named as $\Delta E$) and 17.9 cm (named as $E_{\text{gas}}$). They are separated by an insulating region of 0.1 cm wide created by etching the Ni plate. Rest 1 cm of the plate is etched (0.5 cm on each side) in order to connect it with grid and cathode with the support of an insulating rod. Positive bias is given at
the anode to collect electrons and get energy signal. The very design of $\Delta E$ and $E_{gas}$ anodes is kept in such a way that appreciable energy loss for lower and higher masses takes place within this length. The length of the gas detector and the operable pressure is not enough to stop the recoils of higher elements than C. Therefore in such specific cases SSBD is necessary. A frisch grid made up of fine nickel wire mesh of 99% transparency is kept at a distance of 1.5 cm from the anode with the help of insulating support spacer. The utility of the grid is to eliminate the dependence of pulse amplitude on the position of interaction in the active volume. The cathode, 9.5 cm wide and 26.5 cm long, Ni cladded epoxy plate, is divided into left and right section using a saw tooth geometry, with each saw tooth being 8.2 cm height and 1 cm wide. This special design of the cathode is made for position sensitivity of the detector [8], which can be used to correct the kinematic broadening of the detector, and hence a better energy resolution can be obtained. This plate is given negative bias and the positive ions are collected in this. Frisch grid and cathode are separated by 9.5 cm. This inter-electrode separation is kept in such a way that recoils entering into the active region of the detector should not hit the plates. In this calculation, the angular straggling of the recoils in the gas is also taken into consideration. End part of the electrodes is attached to two Al blocks by teflon screws. Al blocks are tightly screwed with the back plate. The structure of the electrodes is shown in figure 3.5.
The electric field inside the active region of the gas chamber is confined by providing an appropriate potential gradient between cathode to grid.

3.1.3.3 Surface barrier detector

This is a 9.2 cm diameter solid state detector (MSX 65 300, Micron Semiconductor Ltd.) installed after the ionization chamber inside the detector housing. This works as a stop detector for low mass elements (H, He etc.) as it is not possible to stop...
these elements in the gas detector, which requires a very large length or unrealistic gas pressure. The solid state detector is mounted on a circular teflon block which is tightly attached to the back plate. This detector has 10-pin connections, one side connected to the detector (as marked in the figure 3.6) and another side open, from where electrical connections are to be taken out.

![Diagram of SSBD connections](image)

**Figure 3.6: Electrical pin connections of SSBD**

The central two pins marked, as active area is the active detecting medium from where the signal has to be collected. Two pins at the right side of the active area are termed as "back contact", through which the bias is to be given. Two pins at the left side of active area named as "guard ring". Adjacent pins of back contact and guard ring are redundant. Extreme two pins of both the sides are for ground connection.

### 3.1.3.4 Window and its support

Window of the detector (6 cm diameter circle) is a 1.5 μm aluminized mylar foil stretched on a teflon block and supported by Mo coated Ni wire of 70 micron
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thickness. The design of the teflon block with window is shown in figure 3.7. The teflon block is connected to the front flange, inside the detector housing.

![Diagram of teflon block for window support]

Figure 3.7: To the scale diagram of teflon block for window support

In front of the circular window, a square (5 cm x 5 cm) made of copper cladded glass epoxy plate is attached in order to get rid of the edge effect. The design is made in such a way that no dead space exists in between window and the electrode considering the equipotential lines (discussed in 3.1.3.8).

3.1.3.5 Intermediate chamber and mask arrangement

In between detector housing and gate valve an intermediate chamber (shown in fig. 3.4) of 22 cm in length is placed. There are two important purposes of this chamber: (i) to give the bypass connection (described in 3.1.3.6) and (ii) to insert the calibration mask.
3.1.3.6 Gas handling system

Gas handling system for ionization chamber essentially consists of three parts, (i) inlet, (ii) outlet and (iii) bypass. The inlet pipe connection is made from an isobutane cylinder to the detector chamber through a needle valve, which regulates the gas flow from the cylinder to ionization chamber. In any emergency case, this needle valve can be shut off. A dial gauge is connected in the inlet side by a T'-connection to measure the gas pressure (as shown in figure 3.4). The outlet gas connection is taken with a pipe from the detector housing to a rotary pump through similar needle valve as in input side. Outlet pipe is connected to the rotary pump through one end of a T'-connection. Other end of the T'-connection is connected to a valve. This valve is connected to one end of a T'-connection coming from intermediate chamber. A Pirani gauge is connected to the other end of this T' to monitor the pressure of intermediate chamber and detector (when bypass valve is open) and only intermediate chamber (when bypass is closed). A bypass line is connected from detector house to intermediate chamber through a valve. At the time of evacuating the high vacuum chamber and the detector the bypass line is kept open so that the evacuation process takes place throughout and entrance window is not effected. At the time of operation of the detector chamber, the bypass line is kept closed and the optimization of the gas pressure is performed by inlet and outlet regulator valves and the chamber pressure is monitored in the dial
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gauge. The entrance window is capable of withstanding a differential pressure of 50 Torr.

3.1.3.7 Electrical insulation of the detector assembly

It is important to electrically isolate the detector assembly from the rest of the part of the system to avoid unwanted ground pick up. This has been done by connecting the front flange of the detector with the intermediate chamber flange through teflon bushes.

3.1.3.8 Equipotential lines inside the detector

The equipotential lines in between cathode and grid in the optimized condition of bias and gas pressure are calculated using “Charge Simulation Program” [14] and shown in figure 3.8. It is seen that the lines are homogeneous inside the active volume of the detector.

![Figure 3.8: Equipotential lines inside the active volume of the detector](image-url)
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The photograph of the detector connected to the high vacuum chamber and the electrodes mounted on back plate are shown in figures 3.9 and 3.10, respectively.

Figure 3.9: Photograph of the LAPSDT
3.1.4 Test results of the detector

Overall performance of the detector is studied from the following test experiments:

(i) Varying the electric potential of the electrodes and gas pressure, the signal to noise ratio of the detector is checked with $^{252}$Cf-fission fragment source. The electrode potential for optimized signals from the electrodes are, +70 V for anodes, -80 V for cathode and 0 V to grid (grounded) and at pressure of ~14 Torr. It corresponds to 1.1 V/Torr-cm, in the active volume of the detector. In this condition, the signal and noise are checked in the different parts of the detector.
(table 3.1), using a charge sensitive preamplifier (made in house) and EG&G ORTEC linear amplifier (model 572). In table 3.1 signals, noise and % resolution of different parts of the detector are given.

**Table 3.1**

<table>
<thead>
<tr>
<th>Detector Part</th>
<th>Signal</th>
<th>Noise</th>
<th>% Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$</td>
<td>3.5 V</td>
<td>40 mV</td>
<td>1.1%</td>
</tr>
<tr>
<td>$E_{\text{gas}}$</td>
<td>3.4 V</td>
<td>45 mV</td>
<td>1.3%</td>
</tr>
<tr>
<td>Cathode left (CL)</td>
<td>3.2 V</td>
<td>50 mV</td>
<td>1.6%</td>
</tr>
<tr>
<td>Cathode right (CR)</td>
<td>3.2 V</td>
<td>50 mV</td>
<td>1.6%</td>
</tr>
<tr>
<td>SSBD</td>
<td>3.0 V</td>
<td>30 mV</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

From signal to noise ratio, the % resolution is calculated using the formula,

\[
\text{% resolution} = \left( \frac{\text{Noise}}{\text{Signal}} \right) \times 100\%.
\]

(ii) It was ensured that the total counts in different segments ($\Delta E$, $E_{\text{gas}}$ and SSBD) are same. This was tested with $^{241}\text{Am}$ source of $\alpha$-particle.

(iii) Testing of the detector was performed with heavy ion ($\text{Au}^{15+}$, 200 MeV) in ERDA geometry (detail in the section 3.2). The aim of this experiment is to test the performance of the detector for mass discrimination. In order to obtain this, ERDA of amorphous carbon (a-C), Cu$_3$N and Fe/Ni bilayer under 200 MeV Au$^{15+}$...
ion were performed. This covers a wide range of recoil masses to study. The two
dimensional ($\Delta E$ versus $E_{\text{tot}}$) ERDA spectra of a-C, Cu$_3$N and Fe/Ni are given in
figures 3.11, 3.12 and 3.13, respectively. The Si bands corresponding to the spectra
3.11 and 3.12 are from Si and glass substrate respectively.

Figure 3.11: Two dimensional spectrum of a-C
3.12: Two dimensional spectrum of Cu$_3$N

Figure 3.13: Two dimensional spectrum of Fe/Ni
In case of higher masses (Cu, Fe, Ni), the gas pressure has to be changed to 20 Torr for optimum signal.

It is clear from these recoil spectra that the neighboring mass separation in lower mass region (C, N, and O) is distinctly achieved (figure 3.11), whereas for higher masses (Fe, Ni) separation is only at higher recoil energy (figure 3.13).

(iv) X-position signal is obtained with the help of the following formula [8]:

\[ X_{\text{position}} = \frac{CL - CR}{CL + CR} \]  \hspace{1cm} (3.16)

Full width half maxima (FWHM) of this position signal indicates total acceptance of the detector. For better distinction of the 2-D bands of different elements, a software gate is made near the central portion of X-position signal. In figures 3.11 to 3.13, the gated 2-D are shown. However, due to gating on position signal the solid angle remains ~1.4 msr.

The overall performance of the detector can be written as: (i) Low signal to noise ratio, indicating a resolution of ~1% as of energy signals ($\Delta E$, $E_{\text{gas}}$ and SSBD) and ~2% for position signals, (ii) distinct Z-separation in the lower and intermediate mass region (iii) Z-separation for higher masses is well only at higher recoil energy.

Present test is performed with 200 MeV Au ion. The use of 200 MeV Ag ion will increase the recoil energies and the performance of the detector will be better.
3.2 On-line Experiments

For the present study, on-line ERDA technique is employed. In this section, the total experimental set up will be described, followed by on-line ERDA technique, determination of electronic sputtering yield and stoichiometry of the films.

3.2.1 Experimental set up

The total experimental set up can be divided into three parts, (i) Pelletron accelerator, (ii) beam line and high vacuum chamber and (iii) telescope detector.

3.2.1.1 Pelletron accelerator

NSC Pelletron accelerator [15] is a 15 UD tandem electrostatic accelerator capable of accelerating any ion from proton to uranium (except inert gases) up to an energy from 30 to 200 MeV depending on the ion. The accelerator having vertical geometry is installed in an SS tank, which is 26.5 m long and 5.5 in diameter and filed with SF$_6$ as an insulating gas. Inside the tank, there is a high voltage terminal, which is about 1.5 m in diameter and 3.81 m in height. This terminal can be charged to a high potential, which can be varied from 4 to 15 MV. The terminal is connected to the tank vertically through the ceramic Titanium tubes called accelerating tubes. A potential gradient is maintained through these tubes from high voltage terminal to ground at the top and the bottom of the tank. A schematic diagram of the accelerator is shown in figure 3.14. Negative ions from the sputter ion source are injected in the accelerator. These are accelerated towards the terminal. In the terminal, negative ions are stripped off a few electrons, thereby
converted to positive ions, which are further accelerated as they proceed to the bottom of the tank to the ground potential. As a result, the ions emerging out of the accelerator gain energy given by \( E = V_T (q+1) \) MeV, where \( V_T \) is the terminal potential in MV and \( q \) the charge state of the ion after stripping. These high energy ions are then analysed to the required energy with the help of a 90\(^0\) bending magnet.
known as analyser magnet, and are directed to the desired experimental area with the help of a multiport switching magnet.

3.2.1.2 Beam line and high vacuum chamber

The ion gets deflected to +15° angle by switching magnet and comes in the materials science beam line, whose schematic is given in figure 3.3. Beam line is maintained at a vacuum of 1×10⁻⁹ Torr, with the help of ion pumps and getter pumps. With the help of magnetic quadrupole and steerer, the beam is focussed on the target situated at the centre of high vacuum chamber. Beam can be collimated to desired size by a double slit before the chamber. High vacuum SS chamber is a 68-cm diameter and is pumped by a cryo pump based high vacuum system to get an ultimate pressure of 8×10⁻⁷ Torr. The target ladder is put from the top of the chamber and its vertical motion is controlled by a motor. Inside of the chamber is viewed with the help of light and CCD camera through the viewport.

3.2.1.3. Telescope detector

This part of the experimental set up is discussed in detail in the section 3.1.

3.2.2 On-line ERDA

Thin film samples are mounted on a stainless steel ladder kept at the center of the high vacuum chamber. Ion beam current (about 0.1 particle nA (1 particle nA = 6.25×10⁹ ions/sec)) at the sample ladder is measured and is calibrated with secondary electron suppressed Faraday cup. Due to this low current the chance of heating the target material is insignificant. Samples are tilted at 30° with respect to
the incident beam direction. The $\Delta E - E$ telescope detector is used at an angle of $45^0$ to detect the recoils. The $\Delta E$ signal is taken from the anode plate of the ionization chamber ($\Delta E$ detector). Rest of the energy of the recoils $E_{\text{rest}}$, is stopped in the solid state detector ($E$ detector). The signals for $\Delta E$, $E_{\text{rest}}$ and incident ion charge are recorded event by event. The schematic of electronic set up with the telescope detector is shown in figure 3.15.
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The electronic gate is generated from the logical OR mode of ion charge signal and energy signal of the $E$ detector. It is to note here that the electronic signals from all the electrodes and SSBD are adjusted in such a way that they are within the gate. On-line data recording and subsequent off-line analysis is performed with the help of the software FREEDOM developed at NSC. Two-dimensional spectrum of $E_{tot}$ (total energy, $\Delta E + E_{resl}$) versus $\Delta E$ are generated, which provides the discrimination of different $Z$ (figures 3.11 to fig. 3.13). With the help of software, a time to charge histogram is generated. Total charge obtained from the histogram is divided into different bins containing equal charge. Corresponding to charge value, the number of incident ion is determined from the formula,

$$n = \frac{QS}{qe} \times \frac{I_F}{I_L}$$  \hspace{1cm} (3.17)

where, $n$ is the number of ions, $Q$ is the charge value obtained from charge histogram, $S$ is the scale value (nC/pulse) of the current integrator, $q$ is the charge state of incident ion, $e$ is electronic charge, $I_F$ is the current in the faraday cup (i.e. the incident beam current) and $I_L$ is the ladder current (i.e. the current generated in a sample and measured by current integrator). Faraday cup is situated in the beam line before the high vacuum chamber on which $I_F$ is measured. Beam is collimated in X and Y direction by a double-slit placed in-between faraday cup and high vacuum chamber in order to fix its position within an area of 2 mm×3 mm. Ion fluence is estimated in each bin by dividing the number of incident ion by the beam
spot area. The beam spot area in tilted sample is estimated as a product of cross sectional area of beam and $1/\sin 30^\circ$. The charge calibration is rechecked with the Si recoil spectra in each bin.

The experimental parameters of all the experiments carried out in this thesis study are tabulated below:

**Experiment 1 (tables 3.2 and 3.3)**

(a) Sample: 3-G (a-C:H film)

<table>
<thead>
<tr>
<th>Ions and energy (MeV)</th>
<th>Maximum fluence (ions/cm$^2$)</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_a$ (keV/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$^{8+}$, 80</td>
<td>$3\times10^{13}$</td>
<td>8.7</td>
<td>0.012</td>
</tr>
<tr>
<td>Ag$^{13+}$,150</td>
<td>$3\times10^{13}$</td>
<td>12.7</td>
<td>0.036</td>
</tr>
<tr>
<td>Au$^{15+}$,200</td>
<td>$3\times10^{13}$</td>
<td>17.6</td>
<td>0.12</td>
</tr>
</tbody>
</table>

(b) Sample: 2-A (CuO film)

<table>
<thead>
<tr>
<th>Ions and energy (MeV)</th>
<th>Maximum fluence (ions/cm$^2$)</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_a$ (keV/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^{13+}$,150</td>
<td>$3\times10^{13}$</td>
<td>22.0</td>
<td>0.08</td>
</tr>
<tr>
<td>I$^{15+}$, 210</td>
<td>$3\times10^{13}$</td>
<td>25.0</td>
<td>0.09</td>
</tr>
<tr>
<td>Au$^{15+}$, 200</td>
<td>$3\times10^{13}$</td>
<td>30.0</td>
<td>0.27</td>
</tr>
</tbody>
</table>

* In this experiment 210 MeV I$^{15+}$ is delivered from Pelletron accelerator, Ludwig Maximilians University, Munich, Germany.
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Experiment 2 (table 3.4):

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Ion, energy (MeV)</th>
<th>Maximum fluence (ions/cm²)</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_n$ (keV/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-C to 3-F</td>
<td>Ag$^{13+}$, 150</td>
<td>2.25x10$^{12}$</td>
<td>~12.0</td>
<td>~ 0.09</td>
</tr>
</tbody>
</table>

Experiment 3 (table 3.5):

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Ion, energy (MeV)</th>
<th>Maximum fluence (ions/cm²)</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_n$ (keV/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-A to 1-C</td>
<td>Au$^{13+}$, 200</td>
<td>8.0x10$^{13}$</td>
<td>~37.0</td>
<td>~0.35</td>
</tr>
</tbody>
</table>

Experiment 4 (table 3.6):

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Ion, energy (MeV)</th>
<th>Maximum fluence (ions/cm²)</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_n$ (keV/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-A (a-C)</td>
<td>Au$^{15+}$, 200</td>
<td>2.2x10$^{13}$</td>
<td>20.0</td>
<td>0.13</td>
</tr>
<tr>
<td>3-B1 (C$_{60}$)</td>
<td></td>
<td>16.0</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>3-C (a-C:H)</td>
<td></td>
<td>16.0</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>3-H (diamond)</td>
<td></td>
<td>29.8</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>3-I (graphite)</td>
<td></td>
<td>24.2</td>
<td>0.16</td>
<td></td>
</tr>
</tbody>
</table>
**Experiment 5 (tables 3.7 and 3.8):**

(a) Samples: 3-B1 to 3-B6 (C\textsubscript{60} films).

<table>
<thead>
<tr>
<th>Ion and energy (MeV)</th>
<th>Maximum fluence (ions/cm\textsuperscript{2})</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_n$ (keV/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au\textsuperscript{15+}, 200</td>
<td>$3\times10^{13}$</td>
<td>16.0</td>
<td>0.11</td>
</tr>
</tbody>
</table>

(b) Sample: 3-B1

<table>
<thead>
<tr>
<th>Ion and energy (MeV)</th>
<th>Maximum fluence (ions/cm\textsuperscript{2})</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_n$ (keV/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au\textsuperscript{32+}, 200</td>
<td>$3\times10^{13}$</td>
<td>16.0</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*In this experiment samples 3-B1, 3-B4 and 3-B6 are studied at LMU.

**Experiment 6 (table 3.9):**

Sample: 3-B1 (C\textsubscript{60}/Si)

<table>
<thead>
<tr>
<th>Ion and energy (MeV)</th>
<th>Maximum fluence (ions/cm\textsuperscript{2})</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_n$ (keV/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag\textsuperscript{11+}, 130</td>
<td>$2\times10^{13}$</td>
<td>14.6</td>
<td>0.03</td>
</tr>
<tr>
<td>Au\textsuperscript{6+}, 80</td>
<td></td>
<td>14.6</td>
<td>0.29</td>
</tr>
</tbody>
</table>
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Experiment 7 (table 3.10):

Sample: 2-D (SiO₂)

<table>
<thead>
<tr>
<th>Ion and energy (MeV)</th>
<th>Maximum fluence (ions/cm²)</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_a$ (keV/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au^{15+}, 200</td>
<td>$2 \times 10^{14}$</td>
<td>15.8</td>
<td>0.12</td>
</tr>
</tbody>
</table>

*This experiment is performed at LMU.

3.2.3 Determination of electronic sputtering yield

The elemental contents (in atoms/cm²) or areal concentration present in a film is deduced from the integral counts of the recoil energy spectra, with the help of equation 3.2. The measurement error in the calculation of content (in atoms/cm²) is:

$$Error = \frac{\sqrt{A_r}}{A_r} \times 100\%$$  \hspace{1cm} (3.18)

Such elemental contents are then plotted with respect to ion fluence. The electronic sputtering yield or $Y$ (atoms/ion) of any element is determined by using the following formula,

$$Y(\text{atoms/ion}) = \frac{\Delta N(\text{atoms/cm}^2)}{\Delta f(\text{ions/cm}^2)}$$  \hspace{1cm} (3.19)
where, $\Delta N$ is the change in areal concentration (atoms/cm$^2$) at two points (in the initial part of the plot) and $\Delta f$ is the difference in corresponding fluence (ions/cm$^2$) values.

### 3.2.3 Determination of stoichiometry of the films

In order to determine the atomic % of any element, first the areal concentration of all the elements present in the film is determined. After that, the areal concentration of that particular element is divided by the total areal concentration of all the elements and multiplied by 100. Assuming, we have a film containing elements $A$ and $B$, the atomic % of element $A$ can be obtained from the formula,

$$\text{atomic % of } A = \frac{N_A}{N_A + N_B} \times 100\% \tag{3.20}$$

where, $N_A$ and $N_B$ are the areal concentration of $A$ and $B$ respectively.

Stoichiometry is simply determined from the ratio of areal concentration of the elements present in any film.

### 3.3 Catcher technique and sputtering yield measurements of thick targets

This technique is used to determine the sputtering yield of carbon from bulk graphite as on-line ERDA is only applicable for thin films. Several small pieces of size 1.5 cm x 1.5 cm from a Si wafer are used as catcher closely placed (~ 20 mm)
to the graphite target situated at $30^0$ with respect to the beam direction to collect the sputtered carbon from graphite. Schematic of the catcher geometry is shown in figure 3.16.

Subsequently, the concentration of carbon deposited on catcher is analyzed by ERDA. A dummy catcher (attached in opposite side of the ladder) is kept in the chamber during irradiation and later ERDA study is performed on this in order to measure the impurity of carbon at the surface of the Si catchers. The concentration of impurity carbon of dummy catcher is subtracted from the content of carbon.

Figure 3.16: Schematic of the catcher geometry
calculated in actual catcher to get the amount of sputtered carbon from the graphite. This content is then divided by the ion fluence to obtain electronic sputtering yield of carbon from graphite.

3.4 Off-line experiments for characterization of the samples

3.4.1 Grazing angle X-ray diffraction (GAXRD)

The Grazing Angle X-ray Diffraction (GAXRD) study of copper nitride and copper oxide films are performed due to two reasons: (i) to identify the crystalline phases and (ii) to estimate the crystallite size along z direction. The motivation for this study is to explore the influence of size of the crystallite on electronic sputtering. The GAXRD experiments have been performed with the help of SIEMENS diffractometer at IUC-DAEF, Indore.

The purpose of GAXRD is to limit the penetration of X-ray beam and enhance the diffraction pattern of the film with respect to the substrate. Individual crystalline phases are identified by their characteristic diffraction patterns. Such X-ray patterns also reveal information on the orientation and size distribution of the crystallites.

The basis of x-ray diffraction is the Bragg equation, which describes the condition for constructive interference for X-rays scattering from atomic planes of a crystal. The condition of constructive interference is

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

(3.21)
where \( d \) is the interatomic spacing (in Å), \( \theta \) is the angle (in degrees) of diffraction and \( \lambda \) is the wavelength (in Å) of the incident radiation. When this geometric requirement is met, X-rays scattered from a crystalline solid can constructively interfere, producing a diffraction pattern.

A diffractometer can be used to make a diffraction pattern of any crystalline solid. With a diffraction pattern an investigator can identify an unknown substance or mineral, or characterize the atomic-scale structure of an already identified material. Systematic X-ray diffraction data for thousands of mineral species is available. Most of these data are gathered together and published by the JCPDS-International Centre for Diffraction Data.

The diffractometer consists of several parts.

(i) The most important part of the diffractometer is X-ray tube. Inside the tube is a 40,000 V difference between a tungsten filament and copper target. Electrons from the filament are accelerated by this voltage difference and hit the copper target with enough energy to produce the characteristic X-rays of copper. We use one part of the copper spectrum (with a wavelength of 1.54 angstrom) to make the diffraction pattern.

To cool the X-ray tube, clean water is supplied from a chiller. A steady and dependable source of electricity to the diffractometer and its peripherals.

(ii) The computer software (DIFFRAC-AT) controls the diffractometer and records the output for analysis.
(iii) The slit to collimate the X-rays before they reach the sample.

(iv) The sample holder to hold the specimen. Thin film samples are placed in the diffractometer. The collimated X-rays are incident on the sample. The X-rays hit and scatter from the sample. The diffracted X-rays are detected by the detector.

(v) Photomultiplier tube is used as detector. It measures the X-ray intensity. It is mounted on the arm of goniometer, which literally means angle-measuring device. The goniometer is motorized and moves through a range of $2\theta$ angles. Because the detector is connected to the goniometer arm, we can measure the X-ray intensity at any angle to the specimen. That's how the $2\theta$ angles for Bragg's Law is determined. The schematic of X-ray diffraction set-up is shown in figure 3.17.

A diffraction pattern records the X-ray intensity as a function of $2\theta$ angle. Diffraction patterns are prepared as step-scans. To run a step-scan we mount a specimen, set the tube voltage (40 kV) and current (30 mA), and enter the following parameters:

-- A starting $2\theta$ angle ($15^\circ$).
-- A step-size (typically $0.005^\circ$).
-- An ending $2\theta$ angle ($80^\circ$).

Once started, the goniometer moves through its range, stopping at each step for the preset time. The X-ray counts at each step are saved in a file in the computer. In the diffraction pattern, the vertical axis records X-ray intensity. The horizontal axis records angles in degrees $2\theta$. 

The steps that are followed to identify the crystalline phases and the planes and to determine the crystallite size along z direction are:

(i) The diffraction angle corresponding to each peak is noted down.

(ii) From the Bragg’s law the the corresponding $d$ values are calculated.

(iii) In this calculation $n = 1$ is taken (equation 3.21) for lowest angle peak and successively higher for higher angle peaks.
(iv) Corresponding to Bragg angle, the phases are identified with the help of JCPDS data book.

(v) Corresponding to the $d$ values, the miller indices of the crystalline planes for a particular phase are designated from JCPDS data.

(vi) From the width of the diffraction peak the crystallite size along $z$ direction is determined using Scherrer formula [16]:

$$ B = \frac{K\lambda}{R\cos\theta} $$  \hspace{1cm} (3.22)

Where, $B$ is the width of the peak in radians, $K$ is a constant approximately equal to 1, $\lambda$ is the wavelength of monochromatic X-ray beam, $R$ is the crystallite size and $\theta$ is the Bragg angle.

3.4.2 Atomic force microscopy (AFM) for surface morphology

AFM study is performed on Cu$_3$N, Cu$_2$O, CuO and a-C:H films to examine the surface morphology in terms of grain size and surface roughness of the films. The objectives of this study are (i) To characterize the surface of these films and (ii) to understand the dependence of electronic sputtering on the grain size (along XY plane) of the films.

AFM (Digital Instrument, Nanoscope E) study of the films are performed at IUC-DAEF Indore.
AFM is a suitable tool to study the morphology of the non-conducting surfaces with high spatial resolution. The atomic force microscope essentially consists of two parts: optical block and base. The stepper motor, the alignment screws and the scanner are installed within the base, and the sample is mounted on the top of a scanner. The optical block contains a viewing window at the top, a laser diode, mirrors and a photo detector. The cantilever holder is fixed on the top of the alignment screws, with the tip positioned over the sample. The optical microscope or the optical camera attached to the viewing window allows one to observe the cantilever for alignment of the laser beam and for positioning the tip (made of silicon nitride) over the sample surface areas of interest. The Vander waal’s interaction force can be measured as a function of the separation of the tip and the sample surface (a force curve) by multiplying the cantilever force constant ($K_n$) with the cantilever deflection, ($z$). This interaction force deflects the cantilever. A diode laser based feedback detection system monitors and controls the cantilever’s deflection (and hence, the interaction forces). A piezoelectric scanning is used to move the sample under the tip in X-Y direction. A computer based system transforms the data into image and the surface topography of the sample is displayed in the monitor. Schematic of AFM set up is given in figure 3.18 (next page).

Grain size and root mean square surface roughness of the films are determined [17] from AFM images within an area of 500 nm x 500 nm. For the grain size determination, length and breadth of each grain along XY plane is determined. This
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estimated area (using the measured length and breadth of the grain) is equated to \( \pi r^2 \) to get the radius \( (r) \), which is considered as the size of a single grain. The effective grain size is calculated by taking the average of 5 to 6 grains in each AFM frame. The root mean square surface roughness is calculated with the support of the software.

![Schematic of AFM](image)

**Figure 3.18: Schematic of AFM**

### 3.4.3 Raman spectroscopy

Raman spectroscopy is performed on carbon based materials. The motivation behind this study is to understand the structure of the carbon allotropes and to
correlate this with electronic sputtering process. Raman spectroscopy is an ideal tool particularly for carbon based materials as it is sensitive to the transnational symmetry and the lattice vibration [18]. This can also provide information about the crystallite formation and cluster sizes [19]. Since the development of laser, Raman spectroscopy [20] has become an important tool for investigating elementary excitation in solids, for example phonons and plasmons. In Raman spectroscopy, one studies the inelastic scattering of light by the elementary excitations of interest, which is governed by the equations:

\[
\begin{align*}
\hbar \omega_0 - \hbar \omega \pm \hbar \omega(q) &= 0 \\
\hbar k_0 - \hbar k \pm \hbar q + \hbar G &= 0
\end{align*}
\]

(3.23) (3.24)

where \(\omega_0, k_0\) and \(\omega, k\) characterize the incident and scattered light wave frequency and wave vector respectively; \(\omega(q)\) and \(q\) are the angular frequency and wave vector of the elementary excitation, e.g. phonon. The scattered radiation contains, along with the contribution of frequency \(\omega_0\) (the Rayleigh scattering), further terms known as Raman side bands with the frequencies \(\omega_0 \pm \omega(q)\). The plus and minus signs corresponds to the light quanta that have respectively, absorbed the energy of, and lost to, the relevant elementary excitation \([\omega(q), q]\). The lines with frequency smaller than \(\omega_0\) are called Stokes lines; those with higher frequency are the anti-Stokes lines. The schematic of Raman spectroscopy is given in figure 3.19.
Raman spectra of the as grown films (a-C:H, diamond, C\textsubscript{60}) and graphite are recorded in backscattering geometry with U1000 (Jobin Yvon) Raman spectrometer and R649 (Hamamatsu) photomultiplier tube in photon counting mode in the Laser Physics Division of Centre for Advanced Technology, Indore. The laser used is Ar ion laser of continuous wavelength (5145 Å). Raman spectra are taken using line focus with length ~5 mm and width ~50 μm. Path of the Raman scattered light is shown by the dashed line. Structural analysis is performed with the help of following steps:
(i) The Raman peaks are fitted with Lorentzians. The peak width is determined within an experimental error of ±2 cm⁻¹.

(ii) The intensities of the peaks are calculated from the total integral counts under the peak.

(iii) Intensity ratios of different peaks are determined (in a-C:H films).

(iv) Position of each peak is marked within an accuracy of ±0.5 cm⁻¹.

3.4.4 Optical absorption and transmission

Optical absorption study is performed on Cu₃N, Cu₂O and CuO films. The motivation behind this study is to determine the band gap of the films (Cu₃N, Cu₂O and CuO) deposited by rf sputtering. This is used as a supporting experimental tool to characterize these materials and to make sure that these materials are in the category of compound semiconductors [21,22]. Band gap determination is performed in both absorption and transmission mode with light of UV-VIS range.

Optical absorption study is performed by U3300 HITACHI spectrophotometer at NSC, whereas transmission is studied using SHIMATZU 3101 PCUV-VIS spectrophotometer at National Physical Laboratory, New Delhi. The schematic diagram of U3300 HITACHI is shown in figure 3.20.

Here, WI lamp (iodide tungsten lamp (50W)) is used in a visible range and deuterium lamp (D₂) is used in an ultraviolet range. A monochrome light beam divided by the monochromator (Seya-Namioka-type monochromator having
aberration corrected concave diffraction grating) is further branched by a sector mirror into a reference side beam and a sample side beam. It is finally guided to the

Figure 3.20: Schematic diagram of optical absorption set up.

sample compartment. In the sample side, the sample (film on substrate) is kept, whereas in the reference side only the substrate is kept. The transmitted light through the sample is incident to the detector (photo multiplier tube) and the data is recorded in the computer subtracting the reference signal from sample signal.
In the second case, UV-VIS transmission data is recorded in a PC and the coefficient of absorption ($\alpha$) is calculated by the following relation:

$$\alpha = \frac{-1}{d \left(\log T / T_0 \right)}$$  \hspace{1cm} (3.25)

where, $d$ is the film thickness, $T$ is the transmission at different wavelength and $T_0$ is a constant which depends on the refractive index of the substrate ($n_s$) as well as the refractive index of the film ($n_F$) by the relation,

$$T_0 = \frac{16 n_F^2 n_s}{\left(1 + n_F^2 \right) \left(n_s + n_F \right)^2}$$  \hspace{1cm} (3.26)

In the present case, $n_s$ and $n_F$ values are obtained using an ellipsometer (Rudloph Model 43603-200e) with 546 nm wavelength light incident at an angle 70°.

Following steps are taken for the determination of band gap of copper oxide [17] and copper nitride [23] films:

(i) From the wavelength (along X axis) the photon energy is calculated using the formula,

$$E_p = \frac{hc}{\lambda}$$  \hspace{1cm} (3.27)

here, $E_p$ is the photon energy, $h$ is the Planck's constant, $c$ is the velocity of light and $\lambda$ is the wavelength of light.

(ii) The absorption coefficient is plotted as a function of photon energy

(iii) The absorption edge is extrapolated up to the abscissa

(iv) The point at which the extrapolated line cuts abscissa is taken as the band gap as per the standard Tauc's plot technique [24].
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Bibliography

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