Chapter 3

Thin Films – Sample Preparation and Choice of Ion Beams

In the present chapter we give experimental details of C$_{60}$ thin film preparation, the preparation of substrates used to deposit C$_{60}$ thin films and details of the resistive heating technique employed for preparing C$_{60}$ thin films.

3.1 THIN FILM PREPARATION

It has been reported that the choice of substrate is not as crucial for the formation of a crystalline C$_{60}$ films as compared with the thin film formation in other material systems. The reason for this may be due to the fact that the interaction between C$_{60}$ molecules and the substrate is quite weak, and hence the influence of the crystal structure of the substrate on the growing film is small. In contrast to the crystal structure, the substrate temperature has a significant effect on the crystallinity of the growing C$_{60}$ film. Based on the experimental results it has been observed that the crystallinity of the growing C$_{60}$ film is significantly effected by the substrate temperature. Crystalline C$_{60}$ thin films can be obtained only at elevated substrate temperatures. At low growth temperatures, the C$_{60}$ films are always amorphous no matter how well the lattice match between the substrate and the growing thin film [1].

It is known that the primary intermolecular interaction between C$_{60}$ molecules is van der Waals force. Owing to the quasi-spherical shape of individual C$_{60}$ molecules, the C$_{60}$ crystal is orientationally disordered, i.e., each molecule within the crystal can rotate freely around its equilibrium position. Experimental results show that the orientation of an individual C$_{60}$ crystal can be adjusted at an early stage in its growth by the freely rotating
molecules in the crystal. Although the individual C\textsubscript{60} nuclei are randomly oriented on an amorphous substrate at the beginning, they can adjust (relax) their orientations and grow in a preferred orientation if sufficient kinetic energy is provided by an elevated temperature on the substrate. When crystals grow bigger and meet each other, the orientation of each crystal will be affected by its neighbouring crystals since the interaction between the nucleated crystal and the substrate is much weaker than that between the crystals themselves. As a result, the individual C\textsubscript{60} crystals in the thin film will tend to align themselves in a preferred orientation so that they can reside in an energetically more stable position (state). X-ray results show that for thin films of C\textsubscript{60} the orientation is generally either in the \{111\} plane or in the \{220\} plane \cite{1}. However, for the present study we have prepared C\textsubscript{60} films using resistive heating method keeping substrate temperature at room temperature. The films prepared have approximate lattice matching and small grain size. The experimental techniques used for the present study involve study of bulk C\textsubscript{60}. No surface study has been performed which require a film growth with perfect lattice matching for highly crystalline films.

### 3.1.1 SUBSTRATES

The thin films under investigation on SHI irradiation were deposited on Si, quartz and float glass substrates by resistive heating method in the high vacuum deposition system and ultra high vacuum deposition system of the target development laboratory of NSC. The substrates were cleaned prior to deposition in the following sequence. First, in order to remove the organic contaminants from the surface, they were boiled consequently in trichloroethylene (TCE), acetone and methanol for 10 minutes in each chemical. In addition, they were rinsed in deionized(DI) water (resistivity ~ 10 M\textohm-cm) after each step. Lastly, they were dipped in 1 % hydrofluoric acid (HF) solution, to remove native oxide, and rinsed in DI water again. Immediately after cleaning, the substrates were placed in the deposition
chamber. Thin films of $C_{60} \sim 230$ nm were deposited in a vacuum environment of $\sim 10^{-6}$ Torr for the high vacuum deposition system (henceforth referred to as HV samples) and in a vacuum environment of $\sim 10^{-9}$ Torr for ultra high vacuum deposition system (henceforth referred to as UHV samples). The $C_{60}$ films ($\sim 230$ nm) deposited in the high vacuum deposition system had the substrate temperature kept at room temperature whereas the $C_{60}$ films ($\sim 230$ nm) deposited in the ultra high vacuum deposition system had the substrate temperature kept at 200°C. The $C_{60}$ thin films were prepared under different deposition conditions in order to understand the role of substrate and pressure conditions on the crystallinity of the $C_{60}$ films. The thin film preparation was performed at Nuclear Science Center (NSC) New Delhi.

### 3.1.2 RESISTIVE HEATING METHOD

In this method, the evaporative material (material to be evaporated) is kept in a boat in the form of pellets. Materials like $C_{60}$ which are available in the form of powder are pelletized using a ‘die’.

A sufficient amount of heat, in a vacuum environment, provides the necessary vapor pressure for evaporation. Evaporation is done at a rate $\sim 0.1$ nm/s by passing a current of $\sim 75$ A in a Ta boat. Vacuum of $\sim 10^{-7}$ Torr is kept before and during deposition in the high vacuum deposition chamber and a vacuum of $\sim 10^{-9}$ Torr is kept before and during deposition in the ultra high vacuum deposition chamber. The rate of deposition of any vapor on a substrate depends upon the distance of the source relative to the substrate and the condensation coefficient.

The measurement of the film thickness being deposited is accomplished by using a quartz crystal thickness monitor. The monitor operates on the principle of piezoelectric effect. The mass of the deposited film on the crystal surface is determined by the resonant frequency of the quartz crystal.
Schematic diagram and photograph of the high vacuum deposition unit are shown in Figs. 3.1 and 3.2 and those of the ultra high vacuum deposition unit are shown in Figs. 3.3 and 3.4.

Fig. 3.1 Schematic diagram of the High Vacuum Deposition system

Schematic diagram and photograph of the high vacuum deposition unit are shown in Figs. 3.1 and 3.2 and those of the ultra high vacuum deposition unit are shown in Figs. 3.3 and 3.4.
Fig. 3.2 Photograph of High Vacuum Deposition unit at NSC, New Delhi.
Fig. 3.3 Schematic diagram of the Ultra High Vacuum Deposition system
Fig. 3.4 Photograph of the Ultra High Vacuum Deposition unit at NSC, New Delhi.
3.2 ION BEAM CHARACTERISTICS

Thin films of C₆₀ having a thickness of ~ 200 nm were deposited on Si, float glass and quartz substrates. The thickness of the C₆₀ films under study was kept very small as compared to the range of the ions used. The energy of the ions used for irradiation was kept such that the Sₑ value is more than the Sₙ value i.e., the electronic energy loss is dominant for all the ion irradiations. Table 3.1 shows the values of energy, electronic energy loss (Sₑ), nuclear energy loss (Sₙ), range and fluence of the various ions chosen for irradiation on the thin films of C₆₀. These values have been calculated using the code SRIM 2000 [2, 3].

The various ions used for irradiation on the thin films of C₆₀ were chosen such that they have an increasing Sₑ value. Irradiation of these swift heavy ions on the thin films of C₆₀, lead to the formation of defects in the material resulting in various structural transformations. The pristine and the irradiated C₆₀ films were characterized using X-ray diffraction, Raman spectroscopy, Optical Absorption spectroscopy and Electrical conductivity.

Table 3.1 Table showing Sₑ and Sₙ for ions used.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy (MeV)</th>
<th>Electronic Energy Loss (Sₑ) (eV/Å)</th>
<th>Nuclear Energy Loss (Sₙ) (eV/Å)</th>
<th>Range of ion (µm)</th>
<th>Fluence range (ions/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>^{16}O⁵⁺</td>
<td>70</td>
<td>8.095x10³</td>
<td>4.454x10⁻²</td>
<td>62.41</td>
<td>10¹¹ - 10¹⁴</td>
</tr>
<tr>
<td>^{58}Ni¹⁰⁺</td>
<td>110</td>
<td>7.287x10²</td>
<td>9.895x10⁻¹</td>
<td>21.78</td>
<td>10¹¹ - 10¹⁴</td>
</tr>
<tr>
<td>^{197}Au⁸⁺</td>
<td>100</td>
<td>1.292x10³</td>
<td>1.895x10¹</td>
<td>14.95</td>
<td>10¹⁰ - 10¹³</td>
</tr>
</tbody>
</table>

X-ray diffraction technique was employed to identify or characterize the C₆₀ material and study the crystallinity of the C₆₀ film (discussed in section 4.2 of Chapter 4). On any given substrate, C₆₀ is a face centered cubic (f.c.c.) structure with assignment of (111) at 2θ = 10.8, (220) at 2θ = 17.7 and
(311) at $2\theta = 20.8$. JCPDS-ICDD X-ray diffraction data with Ref. No. (44-558) provides a list of all the standard values of $2\theta$ for the bulk C$_{60}$.

Raman spectroscopy technique was employed to characterize the C$_{60}$ material, identify the modifications induced in the irradiated C$_{60}$ films due to SHI’s and to finally study their trends. C$_{60}$ molecule has a most intense mode at 1465 cm$^{-1}$ which corresponds to the pentagonal pinch mode (the A$_g$ internal mode of C$_{60}$). The additional modes around this most prominent mode featured around 1420 cm$^{-1}$ and 1570 cm$^{-1}$ have been identified as one corresponding to the H$_g$ symmetry modes of C$_{60}$. A list of all Raman active modes of C$_{60}$ and its phases is discussed in section 5.3.

Electrical conductivity technique was employed in order to study the electrical transport properties of pristine and irradiated C$_{60}$ films using two probe and four probe arrangements.

Variable temperature resistivity measurements were performed to determine the band gap of C$_{60}$ films which were irradiated to high fluence values.

Optical Absorption spectroscopy method was employed in order to determine the band gap of pristine and various ion irradiated C$_{60}$ films (deposited on quartz substrate). Details of all these techniques is described in subsequent chapters.

The motivations for the present study are to (i) investigate in detail the effect of SHI’s. Thin films of C$_{60}$ deposited under different deposition conditions to study and compare the effect of irradiation and (ii) to study the correlation between S$_{e}$ value of the ion and the transformation of C$_{60}$ to various phases. Finally, an attempt has been made to interpret the results in terms of the total energy deposited in the system.
Bibliography

