Chapter 9

Summary and Concluding Remarks

In the preceding chapters, details concerning the experimental results and their theoretical interpretation have been presented. The main motivation behind this study is to investigate the effect of swift heavy ion irradiation on the structural changes of C\textsubscript{60} thin films and to understand the physical mechanisms involved in the modification of these properties during irradiation.

9.1 Summary

It has already been mentioned that in the swift heavy ion regime the electronic energy loss is about a few hundred times larger than the nuclear energy loss. The implications of this huge electronic energy loss in the thin films of C\textsubscript{60} have been investigated in the present work using techniques like Raman spectroscopy, optical absorption spectroscopy and electrical conductivity.

Initially the HV samples of C\textsubscript{60} grown on Si and float glass substrates and UHV samples of C\textsubscript{60} grown on Si substrates were characterized using x-ray diffraction technique. It was observed that the UHV samples of C\textsubscript{60} had better crystallinity than the HV samples of C\textsubscript{60}. Also the C\textsubscript{60} films grown on Si substrate showed better crystallinity than the C\textsubscript{60} films grown on float glass substrate. Further, swift heavy ion irradiation of HV samples and UHV samples of C\textsubscript{60} was performed using 70 MeV \textsuperscript{16}O\textsuperscript{6+}, 110 MeV \textsuperscript{58}Ni\textsuperscript{10+} and 100 MeV \textsuperscript{197}Au\textsuperscript{8+} ion beams. The fluences for the ion irradiation were chosen between 3 \times 10^{10} - 3 \times 10^{14} ions/cm\textsuperscript{2}.

Raman spectroscopy was used to analyse the structural changes in the pristine and the irradiated samples of C\textsubscript{60}. It has been observed earlier by Raman measurements that swift heavy ion irradiation results in
polymerization of C$_{60}$ thin films at low fluence values. In the present work this effect was studied in detail using swift heavy ions of increasing $S_e$ value. It was observed by us that polymer formation showed an enhanced effect for UHV samples of C$_{60}$ compared to the HV samples of C$_{60}$ on irradiation by SHI’s. The trend of the amount of polymer with increase in fluence was studied in detail. The results show an increase in polymer formation at low fluences, which maximizes at some intermediate value of fluence and finally vanishes at very high fluences. High fluences of SHI irradiation on thin films of C$_{60}$ result in complete transformation of C$_{60}$ to a-C. The damage of C$_{60}$ with increasing fluence value has been theoretically interpreted in terms of damage cross-section. The results show that there is a phase change on irradiation of SHI’s in the thin films of C$_{60}$ indicating two damage cross-sections, one at low fluences where we find a good quantity of polymerized C$_{60}$ and the other at high fluences where we find complete transformation of C$_{60}$ and its polymer modes to a-C.

Optical absorption spectroscopy and electrical conductivity measurements were performed on thin films of C$_{60}$ using SHI’s of O, Ni and Au. The band gap values were estimated using the data of optical absorption spectroscopy and low temperature conductivity measurements. The band gap vs fluence variations were found to fit neatly into exponential decay curves. It can be stated that as the fluence increases the C$_{60}$ samples consist of more than one phase of C (C$_{60}$, polymer C$_{60}$, a-C) with varying $E_g$. So, $E_g$ is a gross parameter for us. In situ conductivity measurements performed on thin films of C$_{60}$ using SHI’s of O, Ni and Au indicate that there is an increase in conductivity of C$_{60}$ samples at high fluences. The fluence at which this increase in conductivity starts depends on the $S_e$ valu of the ion. Lower the $S_e$ value of the ion, higher the fluence required for onset of conductivity in the samples.
9.2 Concluding Remarks

The main conclusions based on the results of x-ray diffraction, Raman spectroscopy, optical absorption spectroscopy and electrical conductivity have been mentioned below.

1. We have crystalline films with face centered cubic (f.c.c.) structure. The results of x-ray diffraction indicate that C\textsubscript{60} films deposited on Si substrate have narrower width of the XRD peaks and larger grain size indicating better crystallinity as compared to C\textsubscript{60} films deposited on float glass substrate.

2. A comparative study of O, Ni and Au SHI’s irradiated on thin films of C\textsubscript{60} helps us to conclude that there is damage of C\textsubscript{60} with increase in fluence At low fluences, C\textsubscript{60} undergoes aggregation resulting in dimer / polymer formation while at high fluences, it completely transforms to amorphous carbon. The additional phases of C\textsubscript{60} observed at low fluences are the dimer and tetragonal phase of C\textsubscript{60} and occasionally the chain polymer phase of C\textsubscript{60}. The polymer mode rises at low fluences, maximizing at a moderate fluence , further decreasing at high fluences and finally vanishing at very high fluences. At high fluences, C\textsubscript{60} and all its polymer modes vanish and there is emergence of a-C. Also, at high fluences we observe formation of SiC at the interface.

3. Substrate dependent studies help us to conclude that polymerization of C\textsubscript{60} has a diminished effect on float glass substrate compared to that on Si substrate. A comparative study of Ni ion irradiated C\textsubscript{60} thin films on float glass and Si(100) substrates reveal that the films deposited on float glass show small amorphous carbon(a-C) features even at low fluences, however a-C features become dominant at higher fluences ~ 10^{13} ions/cm\textsuperscript{2} and above for both the substrates.

4. The deposition conditions also have a prominent role in the crystallinity of the C\textsubscript{60} film. Films deposited in an ultra high vacuum
with substrate temperature kept at 200°C have better crystallinity than C_{60} films deposited in a high vacuum with substrate temperature kept at room temperature. We also observe that the various polymeric phases of C_{60} formed at low fluences on irradiation of SHI’s are more enhanced for the C_{60} films deposited in an ultra high vacuum ~ 10^{-9} Torr keeping substrate temperature at 200°C.

5. We can also conclude that for SHI’s where S_e plays the dominant role, there is correlation between S_e value and the fluences at which various phases come into existence and optimize. The results of optical absorption spectroscopy and resistivity measurements are consistent with those of Raman measurements. The closing of band-gap coincides with total damage of C_{60}. Since a sample with no C_{60} is the same as a-C, it is clear from the experimental results that conductivity of C_{60} is due to presence of a-C and not polymer. As we work with ions having successively higher S_e, the vanishing of C_{60}, vanishing of band gap, rise in conductivity, as well as appearance, maximization and disappearance of polymer, all take place at successively lower fluences. Also, the stability of polymer mode of C_{60} is S_e dependent. In order to obtain maximum polymerization in C_{60} films SHI’s of lower S_e value should be used.

6. A calculation based on the phenomenological model to study the effect of fluence on the damage cross-section of C_{60} shows that over the range of fluence values used by us, the damage cross-section of C_{60} at low and high fluences are different. These damage cross-section of C_{60} can be described well by the following equations.

\[
\frac{N_p}{N_h} = B(1 - e^{-\alpha \phi}) + e^{-\alpha \phi - \sigma \phi} \\
N / N_o \approx (1 - A)e^{-\alpha \phi} + Ae^{-\sigma \phi}
\]  

(9.1)  

(9.2)

where \(N\) denotes the number of C_{60} (unpolymerised and unbroken) molecules per unit area and \(N_p\) denotes that of polymerised buckyballs, after the sample has been exposed to ions with fluence
\( N = N_0 \exp(-\sigma \phi) \)  

where \( N_0 \) is the number of \( C_{60} \) molecules per unit area (proportional to intensity of the characteristic peak of \( C_{60} \), \( A_e \) mode at 1468 cm\(^{-1} \)) in the unirradiated film and \( N \) is the number of \( C_{60} \) molecules (proportional to intensity of the same mode after irradiation) in the film after a fluence \( \phi \), \( \sigma \) is the damage cross section of \( C_{60} \) are intermediate values lying between small and large fluence cross-sections found by equations (9.1) and (9.2).

### 9.3 Future perspective

In the present work an attempt has been made to comprehend the structural changes involved in modification of the electrical and optical properties of \( C_{60} \) induced by swift heavy ion irradiation. The structural changes were identified and interpreted using the technique of Raman spectroscopy. There are several possible extensions of this work some of which are listed below.

- Quantitative information regarding the structural changes of \( C_{60} \) on irradiation of SHI’s has been obtained using only the technique of Raman spectroscopy. Data from other techniques like the optical absorption spectroscopy should also be analysed in detail to study the structural transformations.

- The exponential decay of the band gap of \( C_{60} \) with increasing fluence on irradiation of SHI’s should be explained theoretically.
• The UHV samples should be further studied in detail. Modeling of UHV samples should be done to interpret the resulting structural changes on irradiation of SHI’s.

• The substrate dependence and the different deposition conditions can be used to explain the role of crystallinity in the resulting structural changes of C\textsubscript{60} on irradiation of SHI’s.

• The morphology distribution of the phases of C\textsubscript{60} inside the C\textsubscript{60} thin films on irradiation of SHI’s with increase in fluence should be studied.

The extension of this work along these directions would lead to a better understanding of the various issues related to the phase transformations in C\textsubscript{60} thin films on irradiation of SHI’s. It would open up many more possibilities, with some relevant applications, in this interesting and newly explored field of SHI irradiation of C\textsubscript{60}. 