CHAPTER - 3

Swift Heavy Ions Induced Effects in Conducting Polymer Composites

3.1 Introduction

This chapter outlines a novel technique for the electrochemical synthesis of Ag-polypyrrol (Ag-Ppy) and Au-polyaniline (Au-PANI) composite films.

A two steps electrochemical synthesis process has been applied for the fabrication of Ag-Ppy and Au-PANI composite films. Initially, Ppy and PANI films were electrochemically synthesized by using chronopotentiometry with optimized process parameters on conducting ITO substrate. The prepared composite films were act as working electrode for the decoration of Ag and Au particles on the surface of Ppy and PANI films by using CV technique. These composites were then studied by using SEM, EDAX, XRD and micro-Raman spectroscopy. Later, the composite films of Ag-Ppy and Au-PANI were irradiated under high vacuum (~5×10^{-6} Torr) at room temperature with 40 MeV Li^{3+} and 40 MeV C^{5+} ion beams irradiation at various fluences ranging from 1×10^{11} to 1×10^{13} ions/cm^{2}. Moreover, in the present investigation the presence of silver and gold particles on the surface of Ppy and PANI films has been confirmed by EDAX. Raman and XRD spectra reveal the structural disorderedness after heavy-ion beam irradiation, which is also indicated by the SEM micrographs.

3.2 Electrochemical Synthesis of Ag-Polypyrrol Composites

Electrochemical measurements were carried out using a CHI 660C electrochemical workstation under computer control. The standard three electrode setup was employed in one compartment electrochemical cell. A rectangular conducting ITO sheet of size 20 × 10 × 0.7 mm have been used as a working electrode whereas a platinum sheet of size 20 × 40 × 0.25 mm was used as a counter electrode. The Ag/AgCl electrode has been designated as reference electrode. Electrochemical synthesis of Ppy was carried out on ITO substrate in an aqueous solution of 0.23 M monomer containing 0.55 M para toluene sulphonic acid (pTS) using chronopotentiometry technique. The surface
The decoration of synthesized film was carried out in an aqueous solution of 0.001 M AgNO3 containing 0.05 M KCl solution using cyclic voltammetry between a potential window of -0.3V to +0.8V at a scan rate of 40mVs⁻¹. The thickness of the composite film was ~100 μm.

SHI irradiation was performed using 15 UD Pelletron at the IUAC, New Delhi. An ultra-high vacuum of ~ 5×10⁻⁶ Torr was maintained within the target chamber during the bombardment. Ag/Ppy films were subjected to 40 MeV Li ions irradiation with fluence of 1×10¹¹ to 1×10¹³ions/cm². The electronic ($S_e$) and nuclear ($S_n$) energy loss values for 40 MeV Li³⁺ ions in Ag/Ppy film were calculated 83.05keV/micron and 4.87×10⁻²keV/micron, respectively. The variation of energy loss as a function of ion energy is shown in Figure 3.1. The range of Li ion in this particular experiment is about 287.32μm, thereby indicating that the entire passage of ions through the film is dominated by the electronic energy loss.

![Figure 3.1: Nuclear and Electronic Energy Loss versus 40 MeV Li Ion Beam Energy in Ag-Ppy Composite](image-url)
Scanning electron microscopic images were obtained by using a JEOL JSM-6490LV microscope at 25kV after covering with a thin layer of sputtered gold. The micro-RAMAN investigation has been carried out using Renishaw InVia Raman microscope before and after irradiation of these composites films. All chemicals were procured from Merck and the solutions were prepared in double distilled water.

3.2.1 Results and Discussions

Galvanostatic depositions of Ppy films were carried out with the optimized process parameters. Chronopotentiograms revealed low polymerization potential and good surface morphology. Chronopotentiogram recorded during synthesis of PPy film with optimized process parameters is shown in Figure 3.2.

![Figure 3.2: Chronopotentiogram Recorded During Synthesis of Ppy-pTS Film with Optimized Process Parameters](image)

The experimental studies shows that the simple Ppy films were inserted as working electrode in an 80 ml aqueous solution of AgNO₃ and KCl for 2-sweep segments of CV to modify the surface of polymer film under 40mV/s scan rate in a potential window of -
0.3 to 0.8V (Figure 3.3). The scan rate was rather kept high for the 2-sweep segments in order to uniformly disperse the metal particles on the surface of Ppy. The pair of peaks centered at approximately 0.2V (Ag/AgCl) related with the AgNO₃-dissociation and subsequent deposition of Ag⁺ cations on Ppy film indicates the redox characteristic of Ppy film and Ag⁺ particles. The cathodic peak clearly corresponds to the reduction of Ag⁺ taken up chemically from the solution. The appearance of the peaks indicates the role of the Ppy as a suitable matrix for the Ag-metal particle binding on the surface of Ppy film. During the cathodic sweep, current begins to flow as a result of the reduction of Ag⁺ on the surface layer of the working electrode. For more than 2-sweep segments, the film is completely cemented by Ag⁺ metal particles and its color completely turns to brown after following the range of optimization processes. Modification by Ag⁺ ions on the surface of Ppy film at 40mV/sec scan rate for lesser sweep segments was obtained. The silver cations (Ag⁺) are percolating like uniform grain distribution throughout a smooth polymer matrix. The same is reflected by the optical microscope and SEM images.

Figure 3.3: The Cyclic Voltammogram of Deposition of Ag Particles on Ppy films between -0.3V to 0.8V in a Solution of AgNO₃+KCl Ratio 0.001:0.05 with Scan Rate of 40mV/sec
3.2.2 RAMAN Spectroscopy

The structure of pristine and ion irradiated Ag-Ppy composite films is determined by using the Raman spectroscopy. Argon laser of excitation wave length 514.4nm was used as an excitation source. Raman spectra of pristine and ion irradiated Ag-Ppy composite films are shown in Figure 3.4. The spectra of pristine films of Ag-Ppy composite shows a wide spread antisymmetrical band produced by the superposition of broad D and comparatively sharp G bands which confirms the amorphous nature of carbon structure with the significant degree of sp$^2$ hybridization. These two bands are named as graphite like G and disorder D bands of the disordered carbon structure (Shekhawat et al. 2011). The G mode is associated with the C-C sp$^2$ bonds. The presence of the D band indicates the formation of aromatic rings/clusters in the sp$^2$ phase. The two peaks observed at wave number around 1350 and 1576 cm$^{-1}$ corresponds to the antisymmetrical C-N stretching and C=C stretching modes of pristine Ag-Ppy composite respectively, which in turn shows a good agreement with Xing and Zhao (2007) results.

Figure 3.4: Raman Spectra of Pristine and Ion Irradiated Ag-Ppy Composite Films
The essential Raman parameters to scrutinize carbon bonding are the FWHM of G band and the intensity ratio of D and G bands (I_D/I_G). It is reported that the intensity ratio of D and G bands is the measure of the size of the sp² phase organized in rings of the amorphous carbon. The clustering of sp² phase and the number of carbon hexagon rings are inversely proportional to the optical band gap energy and vice-versa.

After 40 MeV Li³⁺ ion beam irradiation, an overall decrease in the intensity of the bands was observed with the increase in ion fluence. This decline in intensity is due to the significant loss of hydrogen, creation of unsaturated bonds and the formation of gap states through which electron-hole pairs can recombine by thermal energy dissipation. It is also observed that the slope of the Raman spectra decreases with an increase in Li³⁺ ions fluence indicates the reduction in the Raman intensity of the D and G bands.

Moreover, the Raman spectra establish the shifting of D and G bands after heavy-ion irradiation. The band at 1576 cm⁻¹ was shifted to a higher wave number region after irradiation. This happen due to the shortening of conjugation length of Ppy or the Ppy owns a lower doping level. The shift of 13 cm⁻¹ in 1576 cm⁻¹ (pristine) for 1×10¹³ ions/cm² may also imply due to the defects produced in the structure of Ag-Ppy composite films after irradiation. Broadening in the peaks was also observed as a result of irradiation. The reason of broadening of the Raman bands is the formation of an extended system of conjugated bonds, i.e., the formation of defects after irradiation. The values of the peak frequencies, FWHM of both D & G bands and their peak intensities ratio are calculated from the Raman spectra (Table 3.1).

<table>
<thead>
<tr>
<th>Fluence (ions/cm²)</th>
<th>Band Position (cm⁻¹)</th>
<th>Intensity (a.u.)</th>
<th>I_D/I_G</th>
<th>FWHM</th>
<th>C.S. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>G</td>
<td>D</td>
<td>G</td>
<td></td>
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<tr>
<td>0</td>
<td>1350</td>
<td>1576</td>
<td>169542</td>
<td>186373</td>
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<tr>
<td>1×10¹¹</td>
<td>1387</td>
<td>1585</td>
<td>92195</td>
<td>120102</td>
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<tr>
<td>1×10¹²</td>
<td>1410</td>
<td>1585</td>
<td>37598</td>
<td>47442</td>
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<tr>
<td>1×10¹³</td>
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<td>1589</td>
<td>86863</td>
<td>109410</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Table 3.1: Assignments of Band Position for Pristine and Irradiated Samples
The variation of these parameters with ion fluence is shown in Figure 3.5. It is evident from Figure 3.5 that the FWHM of G band decreases at an ion fluence of $1 \times 10^{11}$ ions/cm$^2$ and begins to increases with the increasing fluence. At a low ion fluence of $1 \times 10^{11}$ ions/cm$^2$, no carbon clustering or defects are observed. Interestingly, with the increase in ion fluence, the clustering of carbon atoms increases thereby producing more defects and strain in the composite film, which is also reflected from the broadening of the Raman peaks.

![Figure 3.5: Variation of Peak Positions, FWHM and Ratio between the Peak Intensities of D and G Bands versus the Ion Fluences](image)

It has been reported that the FWHM is susceptible to structural disorder and mainly arises due to the distortion in bond length and bond angle. It is clear from the figure that the intensity ratio of D and G bands ($I_D/I_G$) decrease at a lower ion fluence of $1 \times 10^{11}$ ions/cm$^2$. At $1 \times 10^{12}$ ions/cm$^2$ $I_D/I_G$ is increasing and above this, it remains constant with the change in ion fluence. It has been reported in the literature that $I_D/I_G$ is considered to reflect the size of the aromatic clusters in disordered carbon and it is proportional to the
number of ordered rings and diameter of clusters created by the clustering of these rings after ions irradiation. Therefore, the cluster diameter or net sp² content decreases up to a fluence of $1 \times 10^{11} \text{ ions/cm}^2$. At $1 \times 10^{12} \text{ ions/cm}^2$, it increases and remains constant at higher fluences. The crystallite size more commonly known as particle size of graphitic zones for disorder amorphous carbon materials can be calculated by using $I_D/I_G$ ratio from the relation given by Shekhawat et al. (2011):

$$i.e. \quad L = \frac{4.95}{\frac{I_D}{I_G}}$$

The calculated values of crystallite size are given in Table 3.1. The crystallite size increases at $1 \times 10^{11} \text{ ions/cm}^2$, whereas at $1 \times 10^{12} \text{ ions/cm}^2$ it decreases, above which, it is constant with the change in fluence. The increase in crystallite is due to the formation of some large-size crystallite in the amorphous region of the composite film at $1 \times 10^{11} \text{ ions/cm}^2$.

Figure 3.6: Deconvoluted Raman Spectra of Pristine and Ion Irradiated Ag-Ppy Composite Films at Various Fluences of 40 MeV Li³⁺ Ions
Further, the decrease in crystallite size shows the formation of the disordered system in the composite films at higher ions fluence and has been reported in detail under Chapter 4 and 5 that the broadening of X-ray diffraction peaks associated with the decrease in average crystallite size and crystallinity due to the effect of heavy-ion beam irradiation on polymers.

To get the qualitative estimation of the modifications occurring in the Ag-Ppy composite films due to SHI irradiation, all the Raman spectrums were fitted with Gaussian following background subtraction. Interestingly, after deconvolution with Gaussian fit, the D and G bands were exactly separated out in the spectrum as shown in Figure 3.6. The estimated values for the peak frequencies, the FWHM of both D and G lines, the ratio between their peak intensities and crystallite size are given in Table 3.2.

Table 3.2: Values of Peak Position, Intensity of D and G Bands Calculated from the Deconvoluted Raman and Value of Crystallite Size Calculated from Intensity Ratio of D and G Bands of Ion Irradiated Ag-Ppy Composites

<table>
<thead>
<tr>
<th>Fluence (ions/cm$^2$)</th>
<th>Peak Positions</th>
<th>FWHM</th>
<th>Intensity (a.u.)</th>
<th>I$<em>{D}$/I$</em>{G}$</th>
<th>C.S. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>G</td>
<td>D</td>
<td>G</td>
<td>D</td>
</tr>
<tr>
<td>0</td>
<td>1324</td>
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<td>644</td>
<td>161</td>
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<td>1×10$^{11}$</td>
<td>1452</td>
<td>1678</td>
<td>579</td>
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<tr>
<td>1×10$^{12}$</td>
<td>1775</td>
<td>1485</td>
<td>1739</td>
<td>547</td>
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</tr>
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<td>2000</td>
<td>1485</td>
<td>1385</td>
<td>547</td>
<td>70876</td>
</tr>
</tbody>
</table>

The variation of the peak frequency, the FWHM of both the D and G bands and the ratio between their peak intensities versus ion fluence is shown in Figure 3.7.

It is exciting to examine that the experimental results of the Raman spectra and deconvoluted Raman spectra with Gaussian fitting shows more or less similar behavior. This clearly indicates a structural change after heavy-ion beam irradiation. The peaks, their shifting and broadening observed in Raman spectra reflects the formation of clusters or defects in the composite films after irradiation. The changes are typically because of the transition from electronic processes to thermal processes, which are taking place with the appearance of more disordered composite films surface.
From the above study, it is concluded that there is overall:

- increase in the widths of D and G lines
- downward shift of the G line peak frequency and
- increase in the $I_D/I_G$ intensity ratio for experimental and deconvoluted Raman spectra with increasing ion fluence.

The results may be associated with the presence of distinct morphologies (as viewed in SEM images) or the formation of clusters or defects induced by ion beam irradiation.

### 3.2.3 Scanning Electron Microscopy (SEM)

The SEM images of Ag-Ppy composite films for pristine and ion beam irradiated are shown in Figure 3.8 [A-E]. Figure 3.8 [A] shows the SEM image of pristine Ag-Ppy composite, which point to white dots appearing on the surface of Ppy films suggesting the formation of silver particles. The pristine Ag-Ppy film indicates the spherical humps on the surface of composite film. Interestingly, the metal particles are entangled into the
layers of Ag-Ppy films. After the SHI beam irradiation, the metal particles got dissipated over the whole surface and embedded into the craters. With the increasing fluence of Li$^{3+}$ ion beam, more Ag particles were generated making its surface more decorated with these particles. Further, with increase in ion fluence, the metal particles are incorporated into the craters as shown by the micrographs. During the ion beam irradiation, the hydrogen gas is released, which is responsible for the creation of defects, polymer conjugation and helps in the incorporation of metal particles into the oligomers/monomer units. This enhances the mechanical and conducting properties of Ag-Ppy composites.

Figure 3.8: SEM Images of (A) Pristine and 40 MeV Li$^{3+}$ Ion Irradiated Ag-Ppy Films at Different Fluences (B) 1×$10^{11}$ ions/cm$^2$, (C) 5×$10^{11}$ ions/cm$^2$, (D) 1×$10^{12}$ ions/cm$^2$, (E) 1×$10^{13}$ ions/cm$^2$ and (F) 1×$10^{13}$ ions/cm$^2$ (Magnified Image of Figure (E))
The SEM micrographs of irradiated samples are shown in Figure 3.8 [B-E]. It is evident from the corresponding micrographs that irradiation causes the surface modification of Ag-Ppy composite films. With an increase in ion fluence, the spherical morphology disappears and craters are formed. With the increase in ion fluence, the surface gets saturated with craters and all such craters are formed by the impact of the ion beam. Furthermore, their size increases with an increase in ion fluence. This is clearly visible from the magnified image as shown in Figure 3.8 [F]. Beneath the layers, the craters are formed within the craters, indicates the layer by layer deposition of Ppy films, hence guarantee its adhesivity and proper deposition. This metal polymer attachment results in an intermediate characteristics properties of metal and polymer.

Figure 3.9 shows EDX spectrum of Ag-Ppy composite film. The EDX pattern shows the peak of carbon and silver. The presence of Ag peak strongly indicates that Ag particles are successfully decorated within the Ppy film. The morphological modification observed clearly indicates the effect of heavy ions irradiation. Moreover, the image shows homogeneous nucleation and high porosity thereby indicating its reliability as a sensing material.

![Figure 3.9: EDX Spectra of Silver Particle in Ag-Ppy Composite Film](image)

### 3.2.4 Conclusion

Ag-Ppy composite films have been synthesized successfully with two steps electrochemical synthesis. In order to enhance the structural surface morphology of the synthesized composite films, they were subjected to irradiation at various fluences of...
Li\(^{3+}\) ion beam. A reasonable improvement has been found after irradiation which make them to be used in chemical as well as bio-sensing applications. Raman spectra at various fluences of Li\(^{3+}\) ion beam irradiation shows the broadening of the peaks and decrease in intensity after irradiation, resulting into the formation of conjugation, polarons and bipolarons.

The effect of heavy ion beam irradiation on Ag-Ppy composites is reported for the first time in the present investigation. This shows that the ion irradiation can be used as a unique tool to change the structural properties of the Ag-Ppy composite films.

### 3.3 Electrochemical Synthesis of Au-Polyaniline Composites

Electrochemical measurements are carried out using a CHI 660C electrochemical workstation under computer control. The standard three electrode setup is employed in one compartment electrochemical cell. Planar platinum sheet (20×10×0.25 mm) was used as a working electrode and another platinum sheet (20×40×0.25 mm) is used as a counter electrode. The Ag/AgCl has been used a reference electrode. Electrochemical synthesis of PANI is carried out on platinum substrate in an aqueous solution of 0.23 M monomer containing 0.65 M dodecyl benzenesulphonic acid (DBS) (optimized values) using chronopotentiometry technique. The surface decoration of synthesized film is carried out in an aqueous solution of 0.0007 M HAuCl₄ containing 0.001 M HNO₃ solution using CV between a potential window of -0.4V to +0.7V at a scan rate of 30mV/s. The thickness of the composite film is ~200 μm. All chemicals are procured from Merck and the solutions are prepared in double distilled water.

SHI irradiation is performed using 15 UD Pelletron at the Inter University Accelerator Center (IUAC), New Delhi, India. An ultra-high vacuum (UHV) of ~ 5×10\(^{-6}\) Torr has been maintained within the target chamber during the ion bombardment. Au-PANI films are subjected to 40 MeV C\(^{5+}\) irradiations with fluence of 1×10\(^{11}\) to 1×10\(^{13}\) ions/cm\(^2\). The electronic (S\(_e\)) and nuclear (S\(_n\)) energy loss values for 40 MeV C\(^{5+}\) ions in Au-Pani film are calculated 2.125keV/micron and 9.23×10\(^{-4}\) keV/micron respectively. The range of C\(^{5+}\) ion in this experiment is about 10.58 mm, indicating that the entire passage of ions through the film is dominated by the electronic energy loss.

Scanning electron micrographs are obtained by using a JEOL JSM-6490LV microscope at 25kV after covering with a thin layer of sputtered gold. The structural studies are
carried out by X-ray diffractometer with Cu-K\textalpha radiation (1.54 Å) for a range of Bragg’s angle 2\(\theta\) (20<\(\theta\)<50) at the scan rate of 0.5°/min. The micro-RAMAN investigation has been carried out using Renishaw InVia Raman microscope before and after irradiation of these composites films.

### 3.3.1 Results and Discussions

A chronopotentiometric deposition of PANI film is carried out with the optimized process parameters as shown in Figure 3.10. The chronopotentiogram revealed low polymerization potential and good surface morphology of the film. PANI film has been synthesized in an aqueous solution of 80 ml in the ratio of 0.23:0.65 molar (M) concentration ratios of aniline monomer and DBS respectively. The DBS being the medium size ion supporting electrolyte ensure the stability and homogenous growth rate of polymer film. PANI films used as working electrode are inserted in an 80 ml aqueous solution of HAuCl\textsubscript{4} and KNO\textsubscript{3} in ratio of 0.0005:0.005 M for CV technique (Figure 3.11).

![Figure 3.10: Chronopotentiogram Recorded During Synthesis of PANI Film with Optimized Process Parameters](image)
The solution was run for 4-cycles of CV with potential scan rate of 30mV/s in a potential window of -0.4 to 0.7V (Figure 3.11). The scan rate was kept high for the redox process to occur and to disperse the metal particles uniformly on the surface of PANI film. The CV implies the electrochemical property of reduction of metal particles on the surface of polymer. The cathodic peak centered at approximately 0.25 V (Ag/AgCl) associated with the HAuCl₄ dissociation and subsequent deposition of Au-complex ion on PANI film. This indicates the redox characteristic of PANI and Au-particles. During the redox process in the solution, the ions of AuCl₄⁻ complex protonates the PANI polymer film and formation of free radicals cations is taking place for the reduction of [AuCl₄] complex ions on the polymer surface.

3.3.2 RAMAN Spectroscopy

The structure of the pristine and ion irradiated Au-PANI composite films is determined by using the Raman spectroscopy. Argon laser of excitation wave length 514.4 nm has been used as an excitation source. Figure 3.12 shows the Raman spectra of pristine and ion irradiated Au-PANI composite films within the range of 200-2000 cm⁻¹.
Raman spectra of pristine Au-PANI composite film contain several peaks. These peaks and their respective Raman intensity are given in Table 3.3. The band at 1215 cm\(^{-1}\) are due to C-N stretching mode of polaronic units and in plane deformation of quinine ring. The strong band at 1489 cm\(^{-1}\) is assigned to C=N stretching mode. The bands at 1585 cm\(^{-1}\), is due to the Raman-allowed phonon high frequency. The peak at 1162 cm\(^{-1}\) is due to C-H bending. The band observed at 1489 cm\(^{-1}\) confirms the presence of doped PANI structure and is due to C-C stretching of the benzene ring. The band close to 1170 cm\(^{-1}\) represents the C-H bending vibration in the aromatic ring. The presence of all these bands confirms the formation of Au-PANI composite film.

Due to 40 MeV ion beam irradiation, the peak at 1344 cm\(^{-1}\) become dominant at \(1 \times 10^{11}\) ions/cm\(^2\), while the G peak reduces after heavy ion beam irradiation. The bands at 1585 cm\(^{-1}\) and 1344 cm\(^{-1}\) are named as graphite like G and disorder D bands of the disordered carbon structure. The bands at 1341 cm\(^{-1}\) and 1585 cm\(^{-1}\) corresponds to the
antisymmetrical C-N stretching and C=C stretching mode, respectively. The G band is associated with C-C sp² bonds.

Table 3.3: Assignment of Band Position for Pristine and Ion Irradiated Au-PANI Composite Films

<table>
<thead>
<tr>
<th>Approximate Band Position (cm⁻¹)</th>
<th>Raman Intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pristine 1×10¹¹ 1×10¹² 1×10¹³</td>
</tr>
<tr>
<td></td>
<td>415 417 419 415</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
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<td>- - 1592 -</td>
</tr>
</tbody>
</table>

The essential Raman parameters to scrutinize carbon bonding are the FWHM of G band and the intensity ratio of D and G bands (I_D/I_G). It is reported that the intensity ratio of D and G bands is the measure of the size of the sp² phase organized in rings of the amorphous carbon. The clustering of sp² phase and the number of carbon hexagon rings are inversely proportional to the optical band gap energy and vice-versa.

Overall decrease in the intensity of the bands is observed with the increase in ion fluence (Table 3.3). This decline in intensity is due to the significant creation of unsaturated bonds and the formation of gap states through which electron-hole pairs can recombine by thermal energy dissipation. It is also observed that the slope of the Raman spectra decreases with an increase in C⁵⁺ ions fluence indicates the reduction in the
Raman intensity. The Raman spectra shows the shifting of bands after heavy-ion irradiation, which may be attributed to the shortening of $\pi$ conjugation length i.e. $\pi$-electron delocalization of the PANI composites.

![Figure 3.13: Deconvoluted Raman Spectra of Pristine and Ion Irradiated Au-PANI Composite Films at Various Fluences of 40 MeV C$^{5+}$ Ions](image)

To get the qualitative estimation of the modifications occurring in the Au-PANI composite films due to SHI irradiation, the Raman spectra are fitted with Gaussian following background subtraction. Interestingly, after deconvolution with Gaussian fit, the D and G bands are exactly separated out in the spectrum as shown in Figure 3.13. The estimated values for the peak frequencies, the FWHM of both D and G lines and the ratio between their peak intensities are given in Table 3.4.

It is evident from Table 3.4 that the FWHM of G band increases with an increase in the ion fluence. The broadening of the Raman bands takes place due to the formation of an extended system of conjugated bonds, i.e. the formation of defects after irradiation.
Table 3.4: Assignments of Band Position for Pristine and Ion Irradiated Samples after Deconvolution

<table>
<thead>
<tr>
<th>Fluence (ions/cm²)</th>
<th>Band Position (cm⁻¹)</th>
<th>Intensity (a.u.)</th>
<th>I_D/I_G</th>
<th>FWHM</th>
<th>C. S. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>G</td>
<td>D</td>
<td>G</td>
<td>D</td>
</tr>
<tr>
<td>1×10¹¹</td>
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</tr>
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<td>0.94</td>
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<td>2268</td>
<td>1772</td>
<td>1.27</td>
</tr>
</tbody>
</table>

It is also reported that FWHM is susceptible to structural disorder and principally arises due to the distortion in bond length and bond angle. The intensity ratio of D and G bands (I_D/I_G) decreases at lower ion fluence and at 1×10¹³ ions/cm², I_D/I_G is increasing. It is also mentioned in the literature that I_D/I_G is considered to reflect the size of the aromatic clusters in disordered carbon and is proportional to the number of ordered rings and diameter of clusters created by the clustering of these rings after ions irradiation. Thus, the cluster diameter or net sp² content decreases up to a fluence of 1×10¹² ions/cm² and above which it is increasing.

The crystallite size (C.S.) of graphitic zones for disorder amorphous carbon materials are calculated by using I_D/I_G ratio from the relation given by Shekhawat et al. (2011).

\[ L = \frac{4.95}{I_D/I_G} \]

The calculated values of crystallite size are given in Table 3.4. The crystallite size increases at 1×10¹² ions/cm², whereas at 1×10¹³ ions/cm² it decreases. The increase in crystallite is due to the formation of some large-size crystallite in the amorphous region of the composite film at 1×10¹² ions/cm². Further, the decrease in crystallite size shows the formation of the disordered system in the composite films at higher ions fluence.

3.3.3 X-ray Diffraction Studies

X-ray diffraction spectra of pristine and ion irradiated Au-PANI composite films are shown in Figure 3.14. The peaks at 20~38 and ~43 representing Braggs reflection from
(111) and (200) planes of Au are observed which indicates the presence of Au particles in Au-PANI composite. The peak at 2θ ~23 is attributed to the periodicity of the polymer chain and identify the PANI as a semi crystalline type of material.

**Figure 3.14: XRD Spectra of (A) Pristine and 40 MeV C⁵⁺ Ion Irradiated Au-PANI Films at Different Fluences (B) 1×10¹¹ ions/cm², (C) 1×10¹² ions/cm² and (D) 1×10¹³ ions/cm²**

The broadening of the (111) peak after irradiation can be explained by drop in the size of the Au particles in the Au-PANI composites. The results of these calculations are consistent with the Raman data.

The change in intensity of peaks after irradiation shows a significant change in the structure of the materials. Table 3.5 obviously shows that the integral intensity decreases gradually with an increase of ion fluence. An apparent explanation for the decrease in intensity can be attributed to the decrease in amount of crystalline phase in the samples and the destruction of crystalline structure. This may happen due to the cross linking of molecular chains, which change the regularly arranged crystallites into non arranged ones by forming new bonds between the neighboring chains. Not only this, a increase in full width at half maxima from the diffraction pattern after irradiation

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has also been observed. The behavior is associated with the decrease in crystallinity of the composite films.

Table 3.5: XRD Parameters for Au-PANI Composite Films

<table>
<thead>
<tr>
<th>Fluence (ions/cm²)</th>
<th>$2\theta$ (deg.)</th>
<th>$b$ (deg.)</th>
<th>$R$ (nm)</th>
<th>$d$ (nm)</th>
<th>$\varepsilon$</th>
<th>$I/L^2$ ($\times 10^{17}$) m²</th>
<th>$g$ (%)</th>
<th>C. S., $L$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>38.4</td>
<td>3.75</td>
<td>2.92</td>
<td>2.34</td>
<td>0.88</td>
<td>2.06</td>
<td>10.76</td>
<td>2.2</td>
</tr>
<tr>
<td>$1\times10^{11}$</td>
<td>38.24</td>
<td>1.97</td>
<td>2.93</td>
<td>2.35</td>
<td>0.46</td>
<td>0.51</td>
<td>5.68</td>
<td>4.5</td>
</tr>
<tr>
<td>$1\times10^{12}$</td>
<td>37.51</td>
<td>2.73</td>
<td>2.99</td>
<td>2.39</td>
<td>0.64</td>
<td>0.97</td>
<td>8.0</td>
<td>3.2</td>
</tr>
<tr>
<td>$1\times10^{13}$</td>
<td>38.28</td>
<td>2.85</td>
<td>2.93</td>
<td>2.34</td>
<td>0.67</td>
<td>1.1</td>
<td>8.21</td>
<td>3.0</td>
</tr>
</tbody>
</table>

In order to get the qualitative estimates of the modification occurring in the Au-PANI composite films due to heavy ion beam irradiation, area of the diffraction peaks calculated from simple Gaussian fittings to the data as a function of ion fluences, is presented in Table 3.5. It is very clear from the table that the increase in an area after heavy ion beam irradiation resulting an enhancement of disorderness in the composite structure.

In addition to this, the crystallite size ($L$), interchain separation ($R$), interplanar distance ($d$), micro strain ($\varepsilon$), dislocation density ($\delta$) and distortion parameters ($g$) are calculated by using Equations 2.6 to 2.11 respectively. The structural parameters viz. $L$, $R$, $d$, $\varepsilon$, $\delta$ and $g$ are calculated with respect to the prominent peak of the pristine and irradiated polymer samples and the same is given in Table 3.5.

The crystallite size increases at $1\times10^{11}$ ions/cm², whereas it decreases with an increase in the ion fluence. The increase in crystallite is due to the formation of some large-size crystallite in the amorphous region of the composite film at $1\times10^{11}$ ions/cm². Further, the decrease in crystallite size shows the formation of the disordered system in the composite films at higher ions fluence. Interchain and interplanar distances are marginally changed because of the angle of the peak ($\theta$), which did not vary significantly after irradiation. The micro strain decreases at lower fluence, whereas it increases with the increase of ion fluence. The increase in micro strain is happening because of the misalignment of the atoms or ions. The dislocation density and
distortion parameters are showing an overall increase with an increase in ion fluence. In this case, the crystallite size shows a decrement at higher fluences, which reflects the formation of disordered system in the composite films. The results suggest that the fault probability of Au-PANI composite films increases after irradiation. These results are in good agreement with the Raman analysis.

3.3.4 Scanning Electron Microscopy (SEM)

The SEM images of Au-PANI composite films for pristine and ion beam irradiated are shown in Figure 3.15 [A-D] where Figure [A] indicate the SEM image of pristine Au-PANI film. White spots appearing on the surface of PANI film suggests the formation of gold particles on the surface of PANI film. The pristine Au-PANI film shows a rough surface with porous structure. Interestingly, the metal particles are
entangled into the layers of Au-PANI film. After the SHI beam irradiation, the Au-PANI composite films show the formation of clusters and craters.

### 3.3.5 Conclusion

Au-PANI composite films have been synthesized successfully with two steps electrochemical technique. In order to enhance the structural surface morphology of the synthesized composite films, they were subjected to irradiation at various fluences of C$^{5+}$ ion beam. After irradiation, a reasonable improvement has been found, which indicates their appropriate use in the chemical as well as bio-sensing applications. A Raman spectrum has shown an overall decrease in peak intensity after irradiation which indicates disorderness in the composite films. The XRD spectra were used to calculate structural parameters viz. crystallite size, interchain separation, interplanar distance, micro strain, dislocation density and distortion parameters of the pristine and irradiated composite films. The XRD results show the decrease in crystallite size after irradiation. Micro strain, dislocation density and distortion parameters are increasing with increase in ion fluence. The results obtained are in good agreement with SEM images.