High Electronic Excitation Induced Modifications by 120 MeV Ni^{9+} Ions in Ag-Polypyrrole Composite Films: A Comparative Study

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Abstract: The effect of high electronic excitation triggered swift heavy ion irradiation on the morphological, structural and electrical properties of Ag-polypyrrole (Ag-PPy) composite films is investigated under the influence of by 120 MeV Ni9+ ion beam having fluences ranging from 1×1011 to 3×1012 ions/cm2. The induced modifications were studied by using various characterization techniques, such as, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy. The Raman spectra of Ag-PPy composite films exhibit the anti-symmetrical formation of peaks designated as broad D and comparatively sharp G band. The size of the sp2 phase in the structure was calculated by the intensity ratio in these bands. XRD analysis showed the formation of large size crystallite in the amorphous regions of the composite films with an increase in the ion fluence. SEM images display the symmetrical growth in the surface morphology of the composite films with respect to increasing ion fluence. An attempt has been made to correlate the observed results with previously reported data to make the current investigation more enlightening.

Key words: Ag-PPy composite, heavy ion irradiation, XRD, IV, SEM, raman.

1. Introduction

Conducting polymers (CPs) are receiving widespread attention for numerous applications because their conductivity can be tuned to the metallic regime by a process called doping [1]. Doping process brings tremendous modification in electronic, magnetic, electrical, optical and structural properties of the conducting polymer [2-3]. Doping of polymeric materials is different from that in inorganic or conventional semiconductors. In CPs, doping is simply a charge transfer process during which the doped material gets partially oxidized (p-doped) or reduced (n-doped). The incorporation of metal nano-particles in CPs matrix has modified the structural and physicochemical properties of metal-polymer composites to a greater extent [4]. Two step electrochemical syntheses is a well-designed and well controllable process to fabricate metal conducting polymer composites (MCPCs) and are reported in earlier communication [5-7].

Swift heavy ion (SHI) irradiation is an effective technique to amend the functional properties of metal conducting polymer composites. SHI irradiation creates active sites on the surface of the polymer matrix and which causes structural, morphological changes and modify physiochemical properties of MCPCs. The primary phenomenon associated with ion beam and target material interactions are cross-linking, chain scission. Further, the phenomenon causes mission of atoms, molecules and molecular fragments followed by chemical reaction in the materials by producing radicals and ionised species together with the free or trapped electrons and displaced atoms [8-11].

In our previous group work, we have carried out the detailed investigation of the effects of irradiation on the properties of different conducting and non conducting polymeric materials [12-20]. Recently, the couple of papers are published related to the modifications induced by irradiation on metal-conducting polymer composites [21-25].

The current study deal with the detailed study of the effect of 120 MeV Ni^{9+} ion beams on Ag-PPy composite film. The Ag-PPy composite films are synthesized by using the electrochemical technique. The composite films are characterized by using Raman spectroscopy, X-ray diffraction (XRD), I-V measurement and Scanning electron microscope (SEM) techniques before and after irradiation. The magnitude of the effect of ion beam energy and the effect of irradiated target material during the SHI irradiation are discussed. An attempt is made to study the influence of SHI irradiation on Ag-PPy on the basis of energy absorption and energy dissipation during SHI irradiation.

2. Experimental Details

The Ag-PPy composite films are synthesized using two-step electrochemical technique, having thickness ~20 μm. Details of the synthesis and irradiation process were reported in our previous work [5-7, 21-22]. In this work, the irradiation was performed at different fluences of 120 MeV Ni9+ ions using 15 UD Pelletron at Inter University Accelerator Center (IUAC), New Delhi, India. The electronic (Se), nuclear (Sn) energy loss, and range of incident 120 MeV Ni ion in Ag-PPy were simulated using stopping and range of ions in matter (SRIM) and the values are depicted in Table 1. The energy transported from the incident ion to the target material was governing by electronic process and the nuclear energy loss was quite negligible to be ignored. Scanning electron microscopic images were obtained using a JEOL JSM-6490LV microscope at 25 kV after covered with a thin layer (~10 nm) of sputtered gold. The micro-RAMAN investigation was carried out using Renishaw InVia Raman microscope. XRD spectra of composite film was recorded on a Phillips X-ray diffractometer with Cu-Kα radiation (1.54 A0) for wide range of Bragg's angle 2θ (20< θ<50) at the scanning rate of 10 per minute. I-V characteristics measurements were made using Keithley 2400-C source meter.

Table 1. SRIM Calculated Se, Sn Values and Range of Ions for Ag-PPy Composite Films.

Energy (MeV)	**Ion**	**Electronic Energy Loss (S_e) (keV/ μm)**	**Nuclear Energy Loss (S_n) (keV/μm)**	**Range (μm)**
120	Nickel (Ni^{9+})	5.392×10^3	8.634	29.98

3. Results and Discussion

3.1. Raman Studies of Irradiated Ag-PPy Composites Films

Raman spectra of the pristine and 120 MeV Ni^{9+} ion irradiated Ag-PPy composite films at different fluences are shown in Fig. 1. The comparative changes in the Raman bands are assessed from the relative growth or reduction in the intensity of the Raman peak connected with the functional groups present in the composite system. The Raman peaks of Ag-PPy composite films and their respective Raman intensity are given in Table 2. The bands detected at 1340cm^{-1}, and 1589 cm^{-1} resemble to the antisymmetrical C-N stretching and C=C stretching, respectively. These bands are in good agreement with the reported literature [26]. The peak located at 1045 cm^{-1} for Ag-PPy is assigned to the C-H in-plane deformation of oxidized PPy. The Raman spectra irradiated by 120 MeV Ni^{9+} ions with different fluences is analyzed through the breakup of Raman spectra into the G peak and D peak as shown in Fig. 1. The Raman spectra of Ag-PPy composite films exhibit the anti-symmetrical formation of broad D and comparatively sharp G band. The G band is originated from the ordered hexagon rings made up of conducting Sp_2 bonded carbon, and the D peak is observed for disordered graphites as the clusters of hexagon rings. The bands at 1589 cm^{-1} and 1339 cm^{-1} are named as graphite like G and disorder D bands of the disordered carbon structure. Fig. 1 and Table 3 shows the regular decrease in the intensity of Raman peaks with the increase in ion fluence of Ni beam. The shrinkage in intensity confirms the creation of unsaturated structures and creation of gap states through which electron-hole pairs can recombine by thermal energy deposition. In Table 2, the intensity of G band and D band and their Intensity ratio (ID/IG) are given. The (ID/IG) describes the measure of the size of the Sp_2 phase in the structure. Initial increase in this intensity ratio is due to the formation of sp2 contents or conjugation in carbon cluster with slight increase in ion fluence. However, from ion fluence of $1x10^{12}$ ions/cm^2, the decrease in this intensity ratio is observed, which represents the decrease in Sp_2 content or unsaturated structure and increase in graphite clustering.

Table 2. Values of Peak Intensity of D and G Bands Their Peak Intensity Ratio of D and G Bands of Pristine and Ion Irradiated Ag-PPy Composites.

Fluence ions/cm^2	Intensity of D band (I_D)	Intensity of G band (I_G)	I_D/I_G
Pristine	47149	62578	0.753
1×10^{11}	41501	48764	0.851
3×10^{11}	31090	42196	0.736
1×10^{12}	25199	39012	0.645
3×10^{12}	22491	34493	0.652

Table 3. Assignments of Band Position for Pristine and Irradiated at Highest ion Fluence i.e. 3×10^{12} Ions/cm^2 for Ag-PPy Composite Film.

Approximate band position (cm^{-1})		Intensity (a. u.)	
Pristine	**3×10^{12} ions/cm^2**	**Pristine**	**3×10^{12} ions/cm^2**
1589	1585	62578	34713
1413	1407	43392	22710
1340	1323	45581	20661
1190	1188	31310	12519
1047	1048	28821	12977
985	980	27248	13416

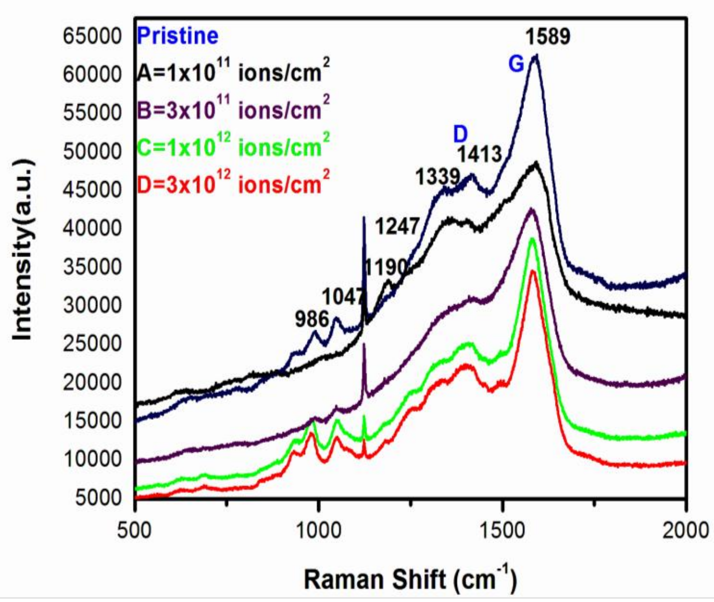

Fig. 1. Raman spectra of pristine and irradiated Ag-PPy composite film irradiated with 120 MeV Ni^{9+} at various fleunces.

3.2. Surface Morphology

The SEM micrographs of Ag-PPy composites films pristine and irradiated by 120 MeV Ni^{9+} ion beam at various fluences are shown in Fig. 2 with their magnified images. The micrograph indicates the change in surface morphology of Ag-PPy composite films. In pristine grain like structures, bulges and bumps on the surface of Ag-PPy composite are observed. At lower 3x1011 ions/cm^2 fluences, no change is observed in grain size and in the morphology of composite film; with increasing fluences the grain size completely vanishes and irregular globular structures with cavities and crater on the surface of Ag-PPy composite film are produced. The swelling in the composite film after irradiation is observed and the grain size changes to irregular globular like structures. At higher fluence 3x10^{12} ions/cm^2 the flower and leaf like symmetrical morphology is also observed. Here, the average diameter of grain size varies from 150 nm to 250 nm during the irradiation process.

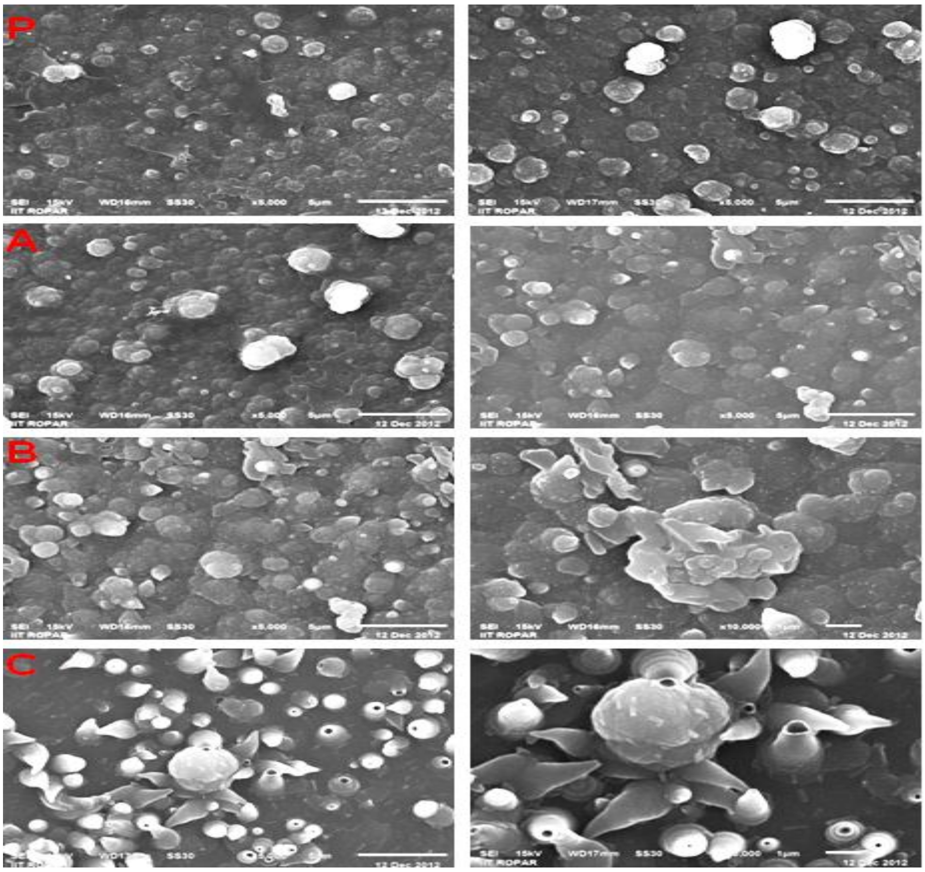

Fig. 2. SEM images of pristine and Ni^{9+} ion irradiated Ag-PPy composite films at (A) 3×10^{11} ions/cm^2, (B) 1×10^{12} ions/cm^2, and (C) 3×10^{12} ions/cm^2 with their magnified images.

3.3. Structural Analysis

The XRD spectra of the Ag-PPy composite films before and after SHI irradiation are recorded and given in Fig. 4. The peak 2θ~21.37 indicates the polymer in a semi-crystalline phase. The peaks at 2θ ~38.13 and ~ 45.44 represents the Bragg's reflection from (111) and (200) planes of Ag respectively, indicating the presence of Ag-particles in the Ag-PPy composite. Irradiation of polymer composite causes degassing in terms of hydrogen, ethane and various other gases. Cross-linking of numerous bonds with neighbouring rings and reorganisation of the polymer composites either leads to the formation of disordered phase or graphite like structure shown by two main G and D and in Raman spectra Fig. 1. This structural rearrangement is due to the condensation of aromatic and unsaturated fragments that produce Sp$_2$ bonded carbon atoms. With the increase in ion fluence, the latent tracks that are produced during the irradiation overlaps which in turn causes the aggregation of π-bonded carbon clusters creating the network of conjugated C=C bonds. The Ni ion beam enhances the structural ordering in Ag-PPy composite due to the formation of graphite like structure after irradiation which is also evident from the decrease in FWHM with increasing fluence as shown in Fig. 4. [32-33].

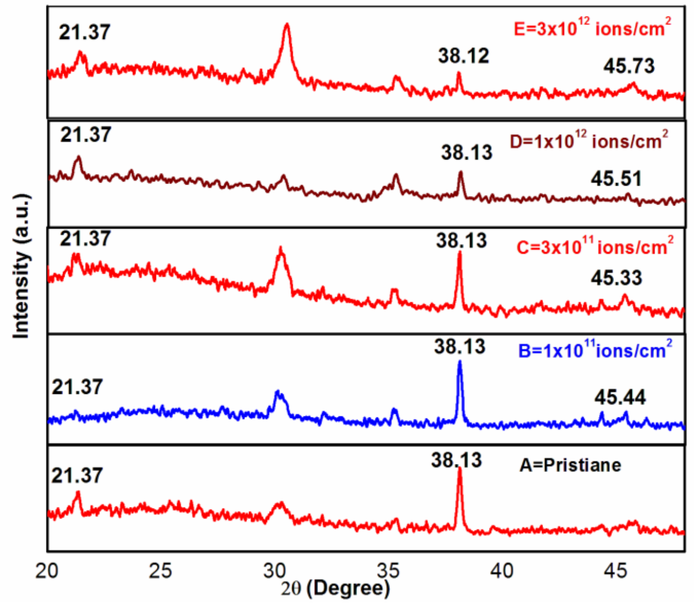

Fig. 3. XRD spectra of pristine and 120MeV Ni^{9+} ion irradiated Ag-PPy film at different fluences (B) = 1×10^{11} ions/cm2, (C) = 3×10^{12} ions/cm^2, (D) = 1×10^{12} ions/cm^2 and (E) = 3×10^{12} ions/cm^2.

4. Conclusions

Structural and ordered modifications are observed in the Ag-PPy composite after irradiation with 120 MeV Ni^{9+} ion beam. SEM shows good morphological alteration after irradiation. At the higher fluences flower, leaf and irregular spherical morphology of the Ag-PPy has been observed which indicates their feasibility to be used in sensing applications. XRD results show the decrease in FWHM with the increase in ion that reflected the formation of more ordered arrangement of atoms in a composite structure. The Raman spectra exhibit a G-band, indicating the graphite like structure. I-V measurements show the enhancement in conductivity at higher fluences due to increase mobility of charge carriers.

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