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Photoluminescence studies on RF plasma-polymerized thin films

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Abstract

Conjugated polymers in the form of thin films play an important role in the field of materials science due to their interesting properties. Polymer thin films find extensive applications in the fabrication of devices, such as light emitting devices, rechargeable batteries, super capacitors, and are used as intermetallic dielectrics and EMI shieldings. Polymer thin films prepared by plasma-polymerization are highly cross-linked, pinhole free, and their permittivity lie in the ultra low *k*-regime. Electronic and photonic applications of plasma-polymerized thin films attracted the attention of various researchers. Modification of polymer thin films by swift heavy ions is well established and ion irradiation of polymers can induce irreversible changes in their structural, electrical, and optical properties. Polyaniline and polyfurfural thin films prepared by RF plasma-polymerization were irradiated with 92 MeV silicon ions for various fluences of 1×10^{11} ions cm^{-2}, 1×10^{12} ions cm^{-2}, and 1×10^{13} ions cm^{-2}. FTIR have been recorded on the pristine and silicon ion irradiated polymer thin films for structural evaluation. Photoluminescence (PL) spectra were recorded for RF plasma-polymerized thin film samples before and after irradiation. In this paper the effect of swift heavy ions on the structural and photoluminescence spectra of plasma-polymerized thin films are investigated.

Keywords: Photoluminescence; Coatings; Polyaniline; Infrared and Raman spectroscopy; Chemical vapour deposition

1. Introduction

Conducting polymers play an important role in the field of material science because of their excellent electrical, optical, and optoelectronic properties. Polymers can be synthesized by chemical, electrochemical, or plasma methods [1,2], and in each case, the composition, morphology, and physical properties of the resulting polymer are strongly dependent on the detailed reaction conditions. Plasma-polymerization is a novel technique for preparing conducting/conjugated polymer thin films [3–5]. The composition of plasma-polymerized films can be tailored with appropriate processing conditions like monomer flow rate, pressure in the chamber, deposition time, and power. The resulting polymer thin film properties are often unique and unobtainable by other polymerization techniques. RF plasma-polymerization [6] is employed for preparing polyaniline and polyfurfural thin films by using aniline and furfural as precursor solutions, respectively. It is also known that for modifying the electrical or optical properties of these films they are doped with iodine, acid groups, etc. Doping of these films modifies the electrical and optical properties [7]. Apart from adding dopants, irradiation of polymer thin films with swift heavy ions also modifies their various properties [8,9]. The swift heavy ions on bombardment results in the breakage of covalent bonds, promotion of cross-linkages, formation of carbon clusters, liberation of volatile species, and in some cases, formation of new chemical bonds [10].

In this paper, the effect of swift heavy ions on the structural and photoluminescence spectra of plasma-polymerized thin films are investigated. Their properties are compared with that of the pristine sample.

2. Experiment

The experimental set up for the preparation of RF plasma-polymerized aniline and furfural thin films is described

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elsewhere [6]. In brief, it consists of a long glass tube of length 50 cm and of diameter around 8 cm with provisions for passing monomer vapour, dopants, and for evacuation. Chemically and ultrasonically cleaned glass substrates with precoated metal electrode was placed inside the glass tube exactly under the space separated by the aluminium foil electrodes, which are capacitively coupled and wrapped around the glass tube separated by a distance of 5 cm. The chamber was evacuated and the monomer (aniline/furfural) was passed into the chamber. Glow discharge was obtained in between the electrodes by applying a high frequency (7–13 MHz) and a current in the range of 60–80 mA. Polyaniline and polyfurfural thin films were coated under optimum conditions. The thickness of the film was measured by employing a homemade device based on Tolansky's interferometric method. The details of this method are cited elsewhere [11].

Polymer thin films of area 1 cm × 1 cm were exposed to 92 MeV Si ions in the material science irradiation facility of the Nuclear Science Centre, New Delhi. The ion beam current was ∼3 pnA (particle nano ampere). The irradiation was carried out at room temperature and under high vacuum. The irradiation fluence was in the range from 10^{11} ions cm^{-2} to 10^{13} ions cm^{-2}, which depends on the time of irradiation and the incident ion current.

The BRUKER EQUINOX 55 FTIR Spectrometer was used for taking IR spectra of monomer, polymer and irradiated polymer thin film samples in the range of 4000–400 cm^{-1}. Photoluminescence (PL) spectra were recorded for RF plasma-polymerized thin film samples before and after irradiation by using He Cd laser [442 nm] and CCD array.

3. Results and discussion

3.1. Structural studies

3.1.1. Polyaniline

The FTIR spectra of pristine and irradiated polyaniline are as shown in Fig. 1, respectively. The peaks at 1656 cm^{-1} and 1423 cm^{-1} correspond to the retention of aromatic rings of polyaniline. The peak at 3207 cm^{-1} shows the vibration of NH group [12]. The peaks at 2883 cm^{-1} and 2834 cm^{-1} are indicative of the CH stretch in polyaniline. The peak at 1059 cm^{-1} is due to CH in plane deformation and CN stretching is observed at 971 cm^{-1}. Substituted benzene ring is also detected from the peaks 783 cm^{-1} and 676 cm^{-1}. Based on the above findings from the FTIR spectra, it is assumed here that hydrogen abstraction is a possibility during plasma-polymerization.

FTIR spectrum of irradiated polyaniline also shows broad peaks. It is observed that there is an intense shift in NH and CH stretching bands with respect to the pristine polyaniline sample. This indicates that the swift heavy ion irradiation disturbs the polymer chain. Also, there is no shift in peaks corresponding to the aromatic ring, which is an indirect evidence to the fact that the swift heavy ion irradiation does not affect all the aromatic rings. However, apart from the fundamental spectral bands, the bands at 2132 cm^{-1} and 2183 cm^{-1} are observed [13] for film bombarded with fluence of 1×10^{11} ions cm^{-2} and 1×10^{13} ions cm^{-2}, respectively. This peak corresponds to C≡C group and the intensity of the peak increases with increase of fluence. This infers that higher fluence play a significant role in modification of these particular thin films. By comparing the FTIR spectra of pristine and irradiated polyaniline, it is clear that the structure of SHI irradiated polyaniline is different from pristine.

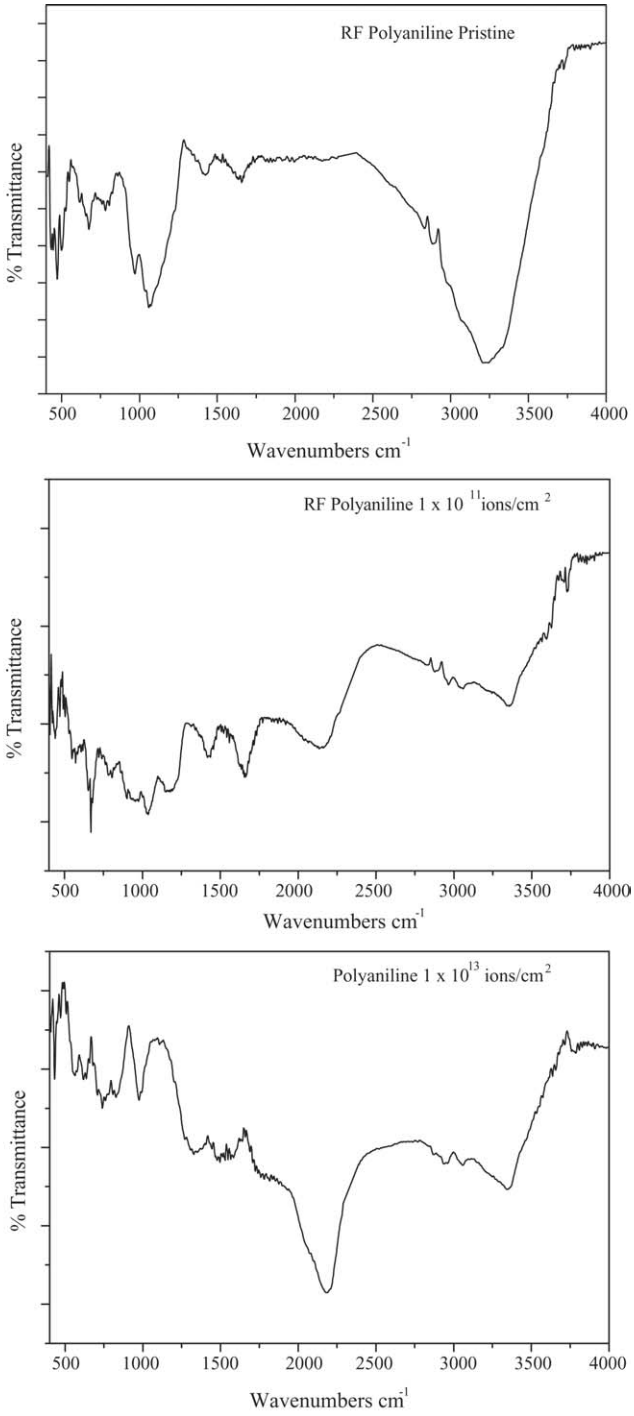

Fig. 1. FTIR spectrum of pristine and SHI irradiated polyaniline thin films.

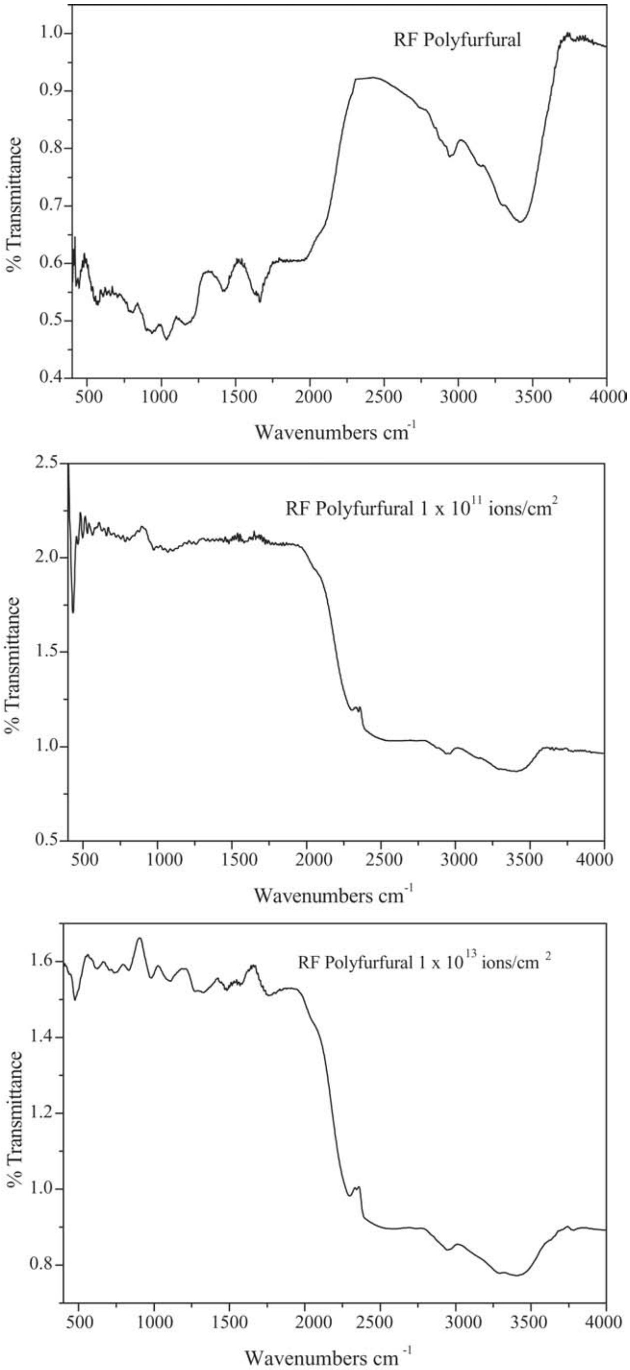

Fig. 2. FTIR spectrum of pristine and SHI irradiated polyfurfural thin films.

3.1.2. Polyfurfural

FTIR spectra of pristine and SHI irradiated polyfurfural are recorded (Fig. 2). The band assignments are compared with the standard monomer furfural values. The peaks at 933 $\mathrm{cm^{-1}}$ and 808 $\mathrm{cm^{-1}}$ in pristine polyfurfural are due to the retention of five-membered ring in the polyfurfural after polymerization too. The peaks at 1159 $\mathrm{cm^{-1}}$ and 1033 $\mathrm{cm^{-1}}$ are indicative of C–O–C asymmetric and symmetric stretch of polyfurfural. The peak at 2938 $\mathrm{cm^{-1}}$ corresponds to the CH stretch [12]. C=O stretch and C=C stretch are observed at 1666 $\mathrm{cm^{-1}}$ and 1411 $\mathrm{cm^{-1}}$, respectively.

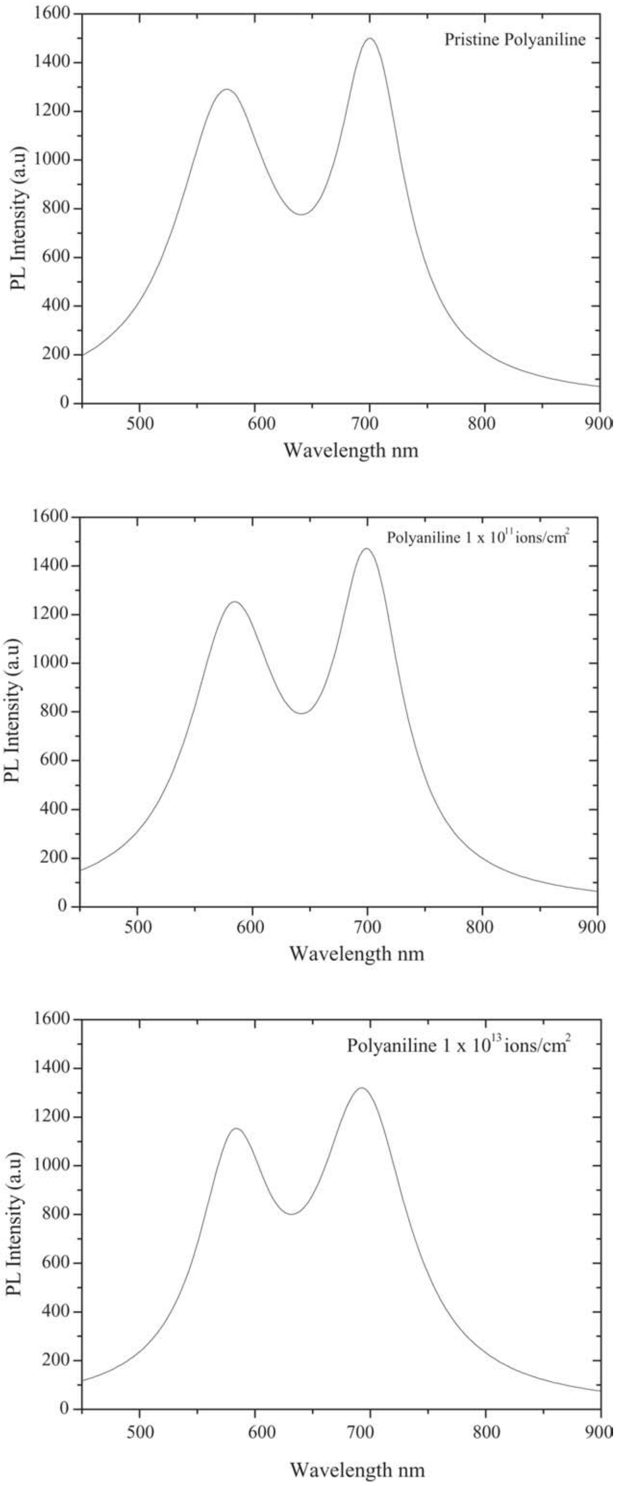

Fig. 3. Photoluminescence spectrum of polyaniline pristine and irradiated thin films.

FTIR spectrum of SHI irradiated polyfurfural thin films are shown in Fig. 2. From the spectrum it is observed that the ion bombardment results in the cleavage of the ring of furfural and leading to a carbonized structure with the elimination of carbon dioxide. The intensity and position of the key bands also changes due to ion irradiation. The FTIR spectrum of the irradiated thin films is very broad and without much significant features.

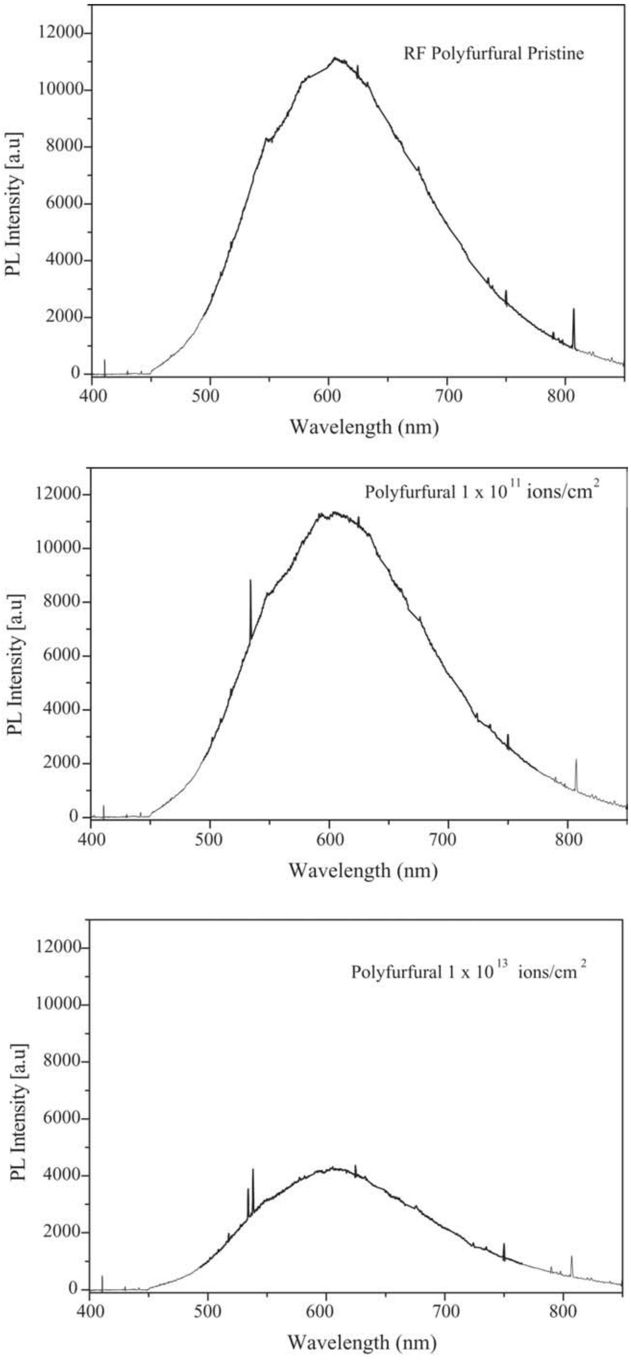

Fig. 4. Photoluminescence spectrum of polyfurfural pristine and irradiated thin films.

This observation also points to the formation of carbonized structure.

3.2. *Photoluminescence studies*

3.2.1. *Polyaniline*

Photoluminescence spectra were recorded for plasma-polymerized aniline samples before and after irradiation and is shown in Fig. 3. The pristine sample exhibits peaks at 575 nm and 680 nm. After irradiation the nature of PL spectrum remains similar but the peak intensity varied slowly with the ion fluence. The peak intensities are compared for different ion fluences. From Fig. 3, it is clearly seen that the intensity of the incident beam decreases with increase of ion fluences.

FTIR spectra indicate that the pristine polyaniline retains the benzene ring and the ring is not opened up. But after irradiation, the ring is opened up because of high-energy ions, which induce structural changes. The rearrangement of bonds as well as the increase of conjugation in the polymer leads the decrease of PL intensity with increase of ion fluence. However, at lower fluence the variation of PL intensity is low, due to the less conjugation, whereas at higher fluence the intensity is decreases more with respect to pristine. This could be due to opening of more benzene rings at higher fluence. This is in conformity with FTIR results.

3.2.2. *Polyfurfural*

Photoluminescence studies on pristine and irradiated polyfurfural were conducted. Fig. 4 shows the photoluminescence response of the polyfurfural samples.

Polyfurfural pristine and irradiated samples exhibited a broad photoluminescence peak centred on 605 nm. It is interesting to note that the peak intensity of the photoluminescence spectrum decreases with increase of ion fluence. This is because of the change in structure. It is clear from the Fig. 4 that there is a decrease in the luminescence intensity. This is primarily caused by absorption of the light in the irradiated polyfurfural thin film also. The fact that we can still observe luminescence on the irradiated thin film demonstrates that the irradiation alter the optical activity of the material.

4. Conclusion

Polyaniline and polyfurfural thin films synthesized by employing RF plasma-polymerization are irradiated successfully with swift heavy silicon ions at different fluences. FTIR spectral results are compared with the standard data and is correlated with the PL studies.

In general, the effect of irradiation in photoluminescence can be viewed in two ways:

(1) the restructuring of the surface chemical species because of the energy deposited through electronic loss during the process of irradiation;
(2) formation of radiation induced defects leading to non-radiative recombination centres.

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References

[1] H.H. Javadi, K.R. Cromack, A.G. MacDiarmid, A.J. Epstein, Phys. Rev. B. 39 (1989) 3579.

[2] Y.G. Wang, J. Joo, C.H. Hsu, A.J. Epstein, Synth. Met. 68 (1995) 207.

[3] F.F. Shi, Surf. Coat. Technol. 82 (1996) 1.

[4] C. Joseph Mathai, S. Saravanan, M.R. Anantharaman, S. Venkatachalam, S. Jayalekshmi, J. Phys. D Appl. Phys. 35 (2002) 240.

[5] P.A. Tanirisa, K.C. Liddell, P.D. Pedrow, M.A. Osman, J. Appl. Polym. Sci. 93 (2004) 1317.

[6] S. Saravanan, C. Joseph Mathai, S. Venkatachalam, M.R. Anantharaman, New J. Phys. 6 (2004) 64.

[7] C. Joseph Mathai, S. Saravanan, M.R. Anantharaman, S. Venkatachalam, S. Jayalekshmi, J. Phys. D Appl. Phys. 35 (2002) 2206.

[8] L. Calcagno, G. Foti, Nucl. Instrum. Methods Phys. Res. (1991) 1153.

[9] L.B. Bridwell, R.E. Giedd, Y.Q. Wang, S.S. Mohite, T. Jahnke, I.M. Brown, C.J. Bedell, C.J. Sofield, Nucl. Instrum. Methods Phys. Res. B 56–57 (1991) 656.

[10] A. Srivastava, T.V. Singh, S. Mule, C.R. Rajan, S. Ponrathnam, Nucl. Instrum. Methods Phys. Res. B 192 (2002) 402.

[11] A. Goswami, Thin Film Fundamentals, New Age International, New Delhi, 1996.

[12] B.S. Furniss, A.J. Hannaford, P.W.G. Smith, A.R. Tatchell, Vogel's Text Book of Practical Organic Chemistry, fifth ed., Addison Wesley, London, 1998, p. 1412.

[13] R.M. Silverstein, G.C. Bassler, C. Terence, Morrill Spectrometric Identification of Organic Compounds, fourth ed., 1980, p. 105.