

Studies on the optical band gap and cluster size of the polyaniline thin films irradiated with swift heavy Si ions

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Abstract

Polyaniline thin films prepared by RF plasma polymerisation were irradiated with 92 MeV Si ions for various fluences of 1×10^{11} , 1×10^{12} and 1×10^{13} ions/cm². FTIR and UV-vis-NIR measurements were carried out on the pristine and Si ion irradiated polyaniline thin films for structural evaluation and optical band gap determination. The effect of swift heavy ions on the structural and optical properties of plasma-polymerised aniline thin film is investigated. Their properties are compared with that of the pristine sample. The FTIR spectrum indicates that the structure of the irradiated sample is altered. The optical studies show that the band gap of irradiated thin film has been considerably modified. This has been attributed to the rearrangement in the ring structure and the formation of C≡C terminals. This results in extended conjugated structure causing reduction in optical band gap.

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1. Introduction

Organic polymers having extended π electron conjugation attracted the attention of various researchers because of their special electrical properties, morphology and crystallinity as compared to other polymers [1]. Conducting polymers, which are stable, processible and have good mechanical properties leads to the possibility of new applications [2,3]. Also conducting polymers were investigated extensively for understanding the underlying physics of the conduction process and for possible applications. Some of the potential devices based on these polymers are organic light emitting diodes, sensors, low-power rechargeable batteries, super capacitors, photovoltaic cells and low dielectric materials in ICs [4–8]. Polyaniline occupies an important position among conducting polymers [9,10] as it is inexpensive, environmentally stable and exhibits high

conductivity. Electronic and photonic properties of polyaniline attracted the attention of researchers due to its potential applications. Available literatures on polyaniline are related to the chemical and electrochemical polymerisation of aniline. Plasma polymerisation is an inexpensive and promising technique for preparing polymer thin films, which are uniform in thickness, pinhole free, and have good adhesive properties. There are many techniques for the preparation of plasma-polymerised thin films. This includes AC, DC and RF. Both ac [8] and rf [11] techniques yield good quality thin films and the process is quite simple. Normally ac plasma-polymerised thin films are insulating in nature and they result in low k thin films [8]. However, rf plasma polymerisation is increasingly being employed for making conducting polymer thin films; these films exhibit enhanced electrical conduction due to the conjugated structure. These are generally thought to be better candidates for fabricating devices. The dopants like iodine, acid groups, etc. can be used for modifying the physical properties of these films [12–14]. Nowadays, irradiation of polymer thin films also plays an important role in modifying the various properties of films [15–17].

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The swift heavy-ion bombardment leads the breakage of covalent bonds, promotion of cross linkages, formation of carbon clusters, liberation of volatile species and in certain cases creation of new chemical bonds [18,19]. They also can induce changes in the electrical conductivity and optical band gap [20,21]. The irradiation of polymer thin films produces carbon clusters too and sometimes induces the formation of nanoclusters, which modifies the physical properties drastically [22,23]. With this motivation, the RF plasma-polymerised aniline thin films have been subjected to swift heavy-ion irradiation. The impact of swift heavy ions on the structural and optical properties of these films is investigated. The influence of various ion fluences on the optical band gap and the production of clusters are also studied.

In this paper, the effect of swift heavy ions on the structural and optical properties of plasma-polymerised aniline thin film is investigated. Dependence of energy density and cluster size of pristine polyaniline is compared with that of the irradiated polyaniline thin film samples.

2. Experimental

RF plasma polymerisation technique is employed for the deposition of polyaniline thin films. Details of the experimental setup are given elsewhere [11]. Polyaniline thin films fabricated by RF plasma polymerisation under optimum conditions are of thicknesses ranging from 1500 to 3000 Å. The thickness of the film was measured by using a homemade device based on Tolansky's interferometric method. The details of this method are cited elsewhere [11].

Polyaniline thin films of area $1 \times 1 \text{ cm}^2$ were exposed to 92 MeV Si ions with the ion beam current $\sim 3 \text{ pA}$ (particle nanoampere) in the material science irradiation facility of the Inter University Accelerator Centre, New Delhi. The irradiation was carried out in the fluence range of 1×10^{11} – $1 \times 10^{13} \text{ ions/cm}^2$, which depends on the time of irradiation and the incident ion current.

IR spectra of monomer aniline, pristine and irradiated polyaniline samples in the range of $4000\text{--}400 \text{ cm}^{-1}$ were recorded by using Bruker EQUINOX 55 FTIR Spectrometer. Hitachi U3300 spectrophotometer was used for recording UV-vis absorption spectrum of the pristine and irradiated polyaniline samples.

3. Results and discussion

3.1. Structural studies

The FTIR spectra of pristine and irradiated polyaniline are reproduced in Fig. 1. The band assignments of the FTIR spectrum of polyaniline are compared with aniline. The extensive studies on the structural properties of pristine and irradiated polyaniline films are reported earlier [24]. The report reveals that the structure of SHI irradiated polyaniline is different from the pristine. The band assignments are given in Table 1. Based on the available

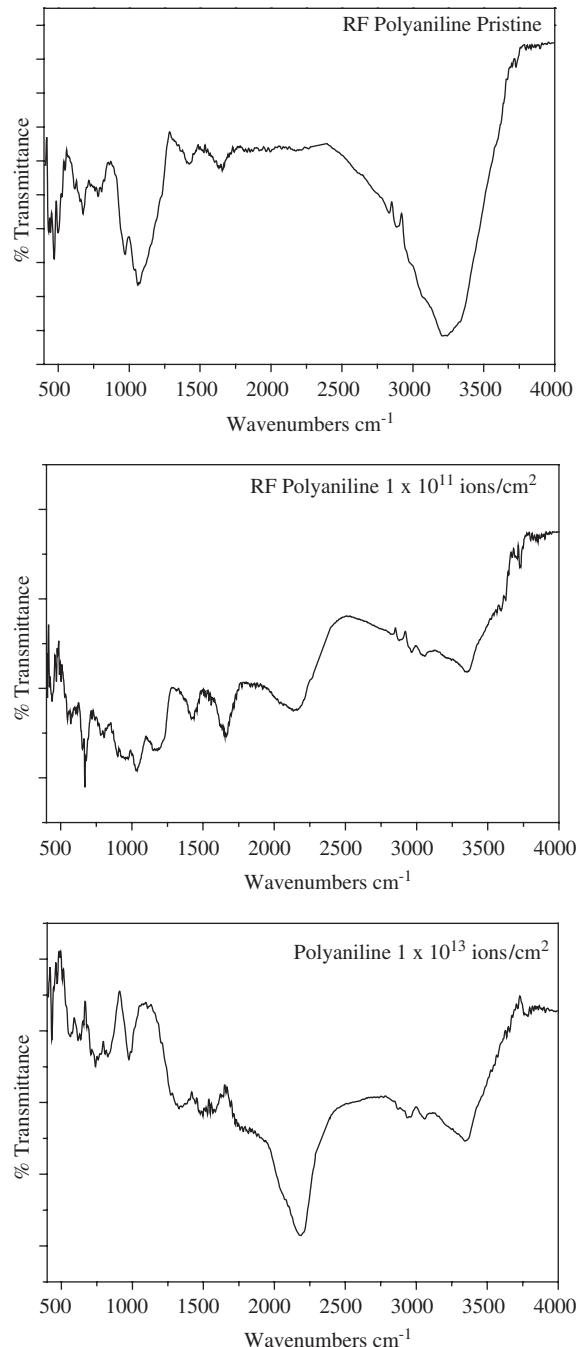


Fig. 1. FTIR spectra of polyaniline pristine and irradiated polyaniline at different fluences [24].

literature, it is inferred that the hydrogen abstraction is a possibility during plasma polymerisation. From FTIR analysis, a plausible structure for RF plasma-polymerised aniline is proposed and is shown in Fig. 2.

The FTIR peaks assigned to the irradiated polyaniline are compared with the pristine polyaniline and are given in Table 1. FTIR spectrum of irradiated polyaniline also shows broad peaks and the detailed explanation is reported [24]. However, in brief, it is observed that there is an intense shift in N–H and C–H 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 the aromatic ring. Apart from these fundamental spectral bands, the bands at 2132 and 2183 cm⁻¹ are observed [25] for film bombarded with fluence of 1×10^{11} and 1×10^{13} ions/cm², respectively. This peak corresponds to C≡C group and the intensity of the peak increases with increase of fluence. Based on the above findings, a probable structure for the irradiated polyaniline is proposed and is shown in Fig. 3.

Table 1
FTIR assignments of polyaniline pristine and irradiated polyaniline at different fluences [24]

Assignment	RF polyaniline		
	Pristine		Irradiated
		1×10^{11} ions/cm ²	1×10^{13} ions/cm ²
N–H vibration	3207	3353	3340
C–H stretch	2883	3058	3058
	2834	2875	2873
C≡C	—	2132	2183
Ring stretch	1656	1664	1565
	1423	1436	1548
C–H in plane deformation	1059	1037	—
C–N stretch	971	973	975
			1326
Substituted benzene ring	783	804	825
	676		

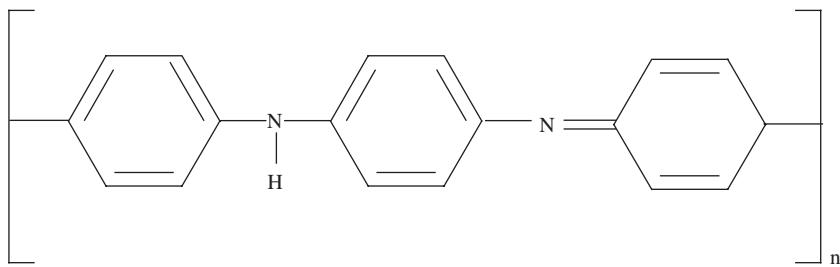


Fig. 2. Structure of RF plasma-polymerised aniline.

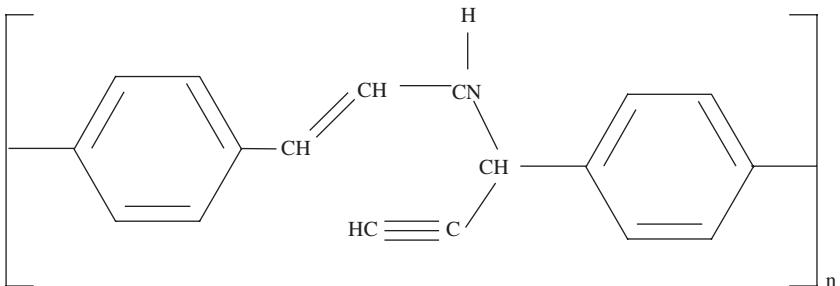


Fig. 3. Structure of RF plasma-polymerised SHI irradiated aniline.

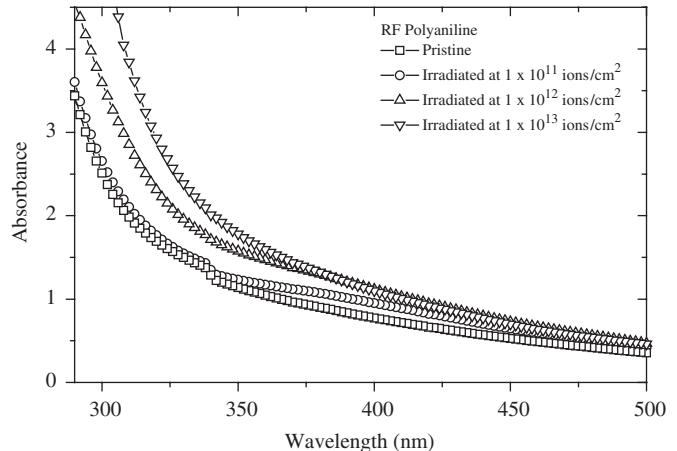


Fig. 4. UV–vis spectra of pristine and irradiated polyaniline.

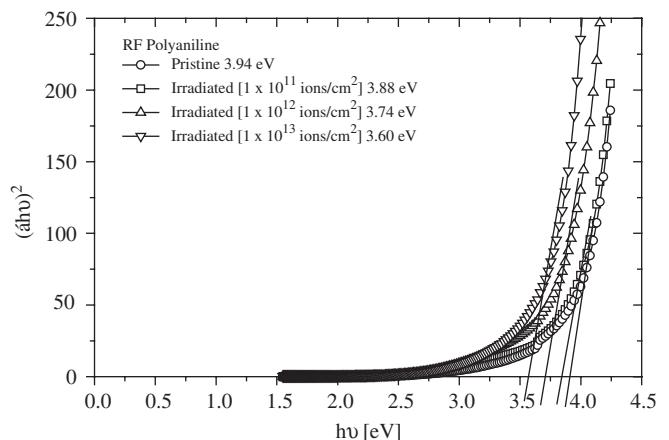


Fig. 5. UV–vis spectra of polyaniline pristine and irradiated polyaniline at different fluences.

Table 2

Optical band gap and cluster sizes for the polyaniline thin films irradiated at different fluences

Polymer	Ion energy (MeV)	Fluence (ions/cm ²)	Energy density (eV/Å ³)	E _g (eV)	Cluster size (no. of carbon atoms)
Polyaniline	92	0	0	3.94	75
		1 × 10 ¹¹	1.56 × 10 ⁻³	3.88	78
		1 × 10 ¹²	1.56 × 10 ⁻²	3.74	84
		1 × 10 ¹³	1.56 × 10 ⁻¹	3.60	90

3.2. Optical studies

The absorbance edge of the UV-vis spectra of pristine and silicon irradiated polyaniline is as shown in Fig. 4. The absorbance in aromatic compounds is due to the π to π^* transition. This is very sensitive to the change in the environment around the phenyl ring [22]. From Fig. 4, it is seen that the absorption edge increases with increase of SHI irradiation. This is due to the increase in conjugated unsaturated bonds.

The photon absorption in many amorphous materials is found to obey the Tauc relation [26], which is of the form

$$\alpha h\nu = B(h\nu - E_g)^n, \quad (1)$$

where α is the absorption coefficient, $h\nu$ the photon energy, B a constant and the index n is related to the distribution of the density of states. The index n has discrete values like 1/2, 3/2, 2 or more depending on whether the transition is direct or indirect and allowed or forbidden, respectively. In the direct and allowed cases, the index $n = 1/2$ whereas for the direct but forbidden cases it is 3/2. But for the indirect and allowed cases $n = 2$ and for the forbidden cases it will be 3 or more.

The absorbance is plotted against the photon energy for polyaniline pristine and the irradiated polyaniline thin films. A satisfactory fit is obtained for $n = 1/2$ showing the existence of direct allowed band gap and is depicted in Fig. 5. The intercept of this plot on the photon energy axis gives the band gap of the samples. From Fig. 5, it is clear that there exists a decrease in band gap for the irradiated thin films. The band gap decreases with increase of ion fluence. It can be seen that while pristine polyaniline exhibits a band gap 3.94 eV, polyaniline irradiated with fluence of 1×10^{13} ions/cm² has a band gap of 3.60 eV. During irradiation hydrogen and other gases are released from the polymeric materials, which causes the enrichment of carbon atoms leading to the formation of hydrogenated amorphous carbon with optical energy gap depending on the H/C atom ratio [19]. The bombardment of swift heavy ions results in rearrangement and bond shifting which leads to ring opening in which C≡C terminals are formed. In this process, the resulting product having conjugated unsaturated bond structure causes the decrease in the optical band gap.

Carbonaceous clusters are generally assumed to induce conductivity and band gap energy is linked to cluster size. According to this, the relation between the number of

carbon hexagon rings in the cluster (M) and the band gap is given by [22]

$$E_g = 2|\beta|M^{-0.5}, \quad (2)$$

where 2β is the band structure energy of a pair of adjacent π sites and β is -2.9 eV for a six-membered carbon ring. But Fink et al. showed that the Robertson equation underestimates the cluster size in irradiated polymers. Hence Fink et al. [23] assumed that the cluster structure is like a buckminsterfullerene structure, i.e., C₆₀ ring instead of C₆ ring. With this assumption they [22] formulated an expression which is given as follows:

$$E_g = \frac{34.3}{\sqrt{N}}, \quad (3)$$

where N is the number of carbon atoms per cluster. By using this the cluster size, number of carbon atoms for an irradiated polyaniline is calculated and is shown in Table 2.

The cluster size for pristine and irradiated polyaniline varies from 75 to 90 carbon atoms. The cluster size in pristine polyaniline is due to the density fluctuations in the polymer structure. Available literature [22] shows that the cluster formation in the case of high-energy heavy ion impact starts at a minimum electronic energy density of around 10^{-3} eV/Å. According to this, the formation of cluster in the polyaniline begins at the ion fluence 1×10^{11} ions/cm². It is also reported that the cluster size increases with increase of complexity of monomeric units. From FTIR studies it is seen that the conjugation of plasma-polymerised aniline increases with increase of ion fluence because of the opening of the benzene ring and formation of C≡C group.

4. Conclusion

Polyaniline thin films prepared by employing RF plasma polymerisation are irradiated successfully with swift heavy silicon ions at different fluences. FTIR spectral results are compared with the standard data and based on the FTIR analysis the structure for the pristine polyaniline and the irradiated polyaniline are proposed. The change in optical band gap for irradiated samples are evaluated and it is found that the optical band gap reduces with increase of fluence. From the absorbance studies, the numbers of clusters for pristine and irradiated polyaniline is calculated.

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