Investigations on pristine and swift heavy ion irradiated plasma polymerized aniline thin films

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1. Introduction

Organic polymers having extended $\pi$ electron conjugation assume significance because of their special electrical properties, morphology and crystallinity compared with other polymers. The synthesis of conducting polymers, which are environmentally, stable, processable, and with good mechanical properties lead to the possibility of new applications. (B. Sanjai et al., 1997; W. R. Salaneck et al., 1991) 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, photo voltaic cells and low dielectric materials in ICs (F. Garten et al., 1996; H. L. Wang et al., 1996; H. Sangodkar et al., 1996; Cartia Arbizzani et al., 1991; C. Joseph Mathai et al., 2002; S. Saravanan et al., 2004). Polyaniline occupies an important position among the conducting polymers (Alan G. MacDiarmid, 1997; H. L. Wang et al., 1996) as it is inexpensive, environmentally stable and exhibit high conductivity. Plasma polymerization is one of the novel techniques for preparing polymer thin films (C. Joseph Mathai et al., 2002; S. Saravanan et al., 2004). Thin films prepared by employing this technique are pin - hole free, uniform in thickness cross - linked and thermally stable. The method of plasma polymerization employs ac/rf/dc and pulsed techniques. Among these, rf plasma polymerization needs special mention since it yields conjugate structures of the polymers, which are supposed to be essential for making conducting thin films. Structural, optical and electrical properties can be modified when it is doped with appropriate dopants (Xing Rong Zeng et al., 1997; C. Joseph Mathai et al., 2002). Apart from adding dopants, irradiation of polymer thin films with swift heavy ions also modifies their various properties (L. Calcagno et al., 1991; Lynn B. Bridwell et al., 1991; J. Davehas et al., 1991; S. Saravanan et al., 2005; S. Saravanan et al., 2007). These swift heavy ions on bombardment results in the breaking of covalent bonds, promotion of cross linkages, formation of carbon clusters, liberation of volatile species and in some cases formation of new chemical bonds (A. Srivastava et al., 2002; Zhiyong Zhu et al., 1992). They also can induce changes in the electrical conductivity and optical band gap (H. S. Virk et al., 2001; M. Gaafar, 2001).
In this chapter fabrication and characterisation of RF plasma polymerised aniline thin films are described. The changes in structural, optical, morphological and electrical properties of pristine polyaniline are compared with the irradiated polyaniline.

2. Background and Experiments

Preparation of polyaniline thin films by employing AC plasma polymerisation and RF plasma polymerisation techniques are reported elsewhere (C. Joseph Mathai et al., 2002; S. Saravanan et al., 2004; U S Sajeev et al. 2006). Formation of polymeric materials under the influence of partially ionised gas is termed as plasma polymerisation. Since it involves the use of an electric glow discharge in vacuum it is also known as glow discharge polymerisation. Plasma polymerisation can take a variety of forms depending on the monomers and molecular fragments deposited on the surface. With appropriate monomer and operating conditions thin polymer films consisting of hydrocarbons, long polymeric chain consisting of linked carbon atoms and highly cross-linked carbon or hydrogen atoms will be deposited (C. Joseph Mathai et al., 2002; S. Saravanan et al., 2004; U S Sajeev et al. 2006).

Polyaniline thin films are prepared using RF plasma polymerisation technique. The experimental set up for the preparation of RF plasma polymerised aniline is shown in Figure 1. (S. Saravanan et al., 2004) It consists of a long glass tube of length 50cm and of diameter around 8cm with provisions for passing monomer vapour, dopants and for evacuation. Chemically and ultrasonically cleaned glass substrates 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 5cm. The chamber was evacuated $(10^{-2}$ Torr) and the monomer was admitted into the chamber. Glow discharge was obtained in between the electrodes by applying a high frequency (7-13MHz) and a current in the range of 60-80mA. The processing parameters are optimised and films were prepared under optimum conditions (S. Saravanan et al., 2004).

![RF plasma polymerisation set up](image.png)

Fig. 1. RF plasma polymerisation set up (S. Saravanan et al., 2004)

These coated thin films were shifted to a metal coating unit for coating the counter electrode. The aluminium electrode was coated by evaporating high purity aluminium wire under high vacuum. $(8 \times 10^{-5}$ Torr) These films were in the sandwich form of cross sectional area.
2.5 \times 10^{-5} \text{ m}^2. The thickness of the film was measured by a homemade setup employing Tolansky’s interferometric method (A. Goswami, 1996).

RF plasma polymerised aniline thin films of area 1 x 1 cm$^2$ 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 \sim 3\text{pna} (particle nano ampere). The irradiation was carried out at room temperature and under high vacuum. The irradiation fluence was in the range of $10^{11}$-$10^{13}$ ions/cm$^2$, which depends on the time of irradiation and the incident ion current. (S. Saravanan et al., 2005)

The BRUKER EQUINOX 55 FTIR Spectrometer was used for taking IR spectra of monomer aniline, pristine polyaniline and irradiated polyaniline samples in the range of 4000 - 400 cm$^{-1}$. UV Vis absorption and PL studies were carried out on these pristine and irradiated samples by using Hitachi U3300 spectrophotometer and He Cd laser with CCD array respectively. Capacitance and dielectric loss were measured by employing HP 4192A impedance analyser and a homemade dielectric cell in the frequency range of 100 Hz to 1 MHz at room temperature for pristine and irradiated polyaniline thin films. Dielectric constant was calculated from the known values of capacitance, thickness and the area of the sample. These measurements were carried out under dynamic vacuum.

### 3. Structural Studies

The FTIR spectra of aniline, polyaniline and irradiated polyaniline are as shown in Figure 1.A and B (S. Saravanan et al., 2005). The band assignments of the FTIR spectrum of polyaniline are given in Table 1. The peaks at 1656 cm$^{-1}$ and 1423 cm$^{-1}$ correspond to the retention of aromatic ring of polyaniline. The peak at 3207 cm$^{-1}$ shows the vibration of NH group (B. S. Furniss et al., 1998). 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$^{-1}$.

![FTIR Spectrum of Monomer aniline](https://www.intechopen.com)

Fig. 2. A. FTIR Spectrum of Monomer aniline
From the FTIR spectrum of polyaniline it is clear that the plasma-polymerised aniline is highly disordered. Based on the above discussion and from available literature it is inferred that the hydrogen abstraction is a possibility during plasma polymerisation. From FTIR analysis a plausible structure for plasma polymerised aniline is proposed and is shown in Figure 3 (S. Saravanan et al., 2008).

Table 1. FTIR assignments of Polyaniline Pristine and irradiated polyaniline at different fluences

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Pristine</th>
<th>RF Polyaniline</th>
<th>Irradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 x 10^{11} ions/cm²</td>
<td>1 x 10^{13} ions/cm²</td>
</tr>
<tr>
<td>N-H Vibration</td>
<td>3207</td>
<td>3353</td>
<td>3340</td>
</tr>
<tr>
<td>C-H Stretch</td>
<td>2883, 2834</td>
<td>3058, 2875</td>
<td>3058, 2873</td>
</tr>
<tr>
<td>C ≡ C</td>
<td>-</td>
<td>2132</td>
<td>2183</td>
</tr>
<tr>
<td>Ring Stretch</td>
<td>1656, 1423</td>
<td>1664, 1436</td>
<td>1565, 1548, 1444</td>
</tr>
<tr>
<td>CH in plane deformation</td>
<td>1059</td>
<td>1037</td>
<td></td>
</tr>
<tr>
<td>C-N Stretch</td>
<td>971</td>
<td>973</td>
<td>975, 1326</td>
</tr>
<tr>
<td>CH Out of plane deformation</td>
<td>783</td>
<td>804</td>
<td>825</td>
</tr>
</tbody>
</table>
Investigations on pristine and swift heavy ion irradiated plasma polymerized aniline thin films

Fig. 3. Tentative structure of RF plasma polymerised aniline

From the FTIR spectrum, peaks assigned to the irradiated polyaniline are tabulated in Table 1. FTIR spectrum of polyaniline irradiated with swift heavy ions also shows broad peaks. From the spectrum, it can be seen that there is intense shift in NH stretching and CH stretching bands with respect to the polyaniline pristine. This indicates that the swift heavy ion irradiation disturbs the polymer chain. Also there is no intense shift in peaks corresponding to the aromatic ring, which is indirect evidence to the fact that the swift heavy ion irradiation doesn’t affect the aromatic ring. Apart from these fundamental spectral bands, the bands at 2132 cm\(^{-1}\) and 2183 cm\(^{-1}\) are observed (Robert M. Silverstein, et al., 1980) for films bombarded with fluence of \(1 \times 10^{11}\) ions/cm\(^2\) and \(1 \times 10^{13}\) ions/cm\(^2\) respectively. This peak corresponds to the \(C \equiv C\) group. The intensity of the peak increases with increase of fluence. Based on this a tentative structure for the irradiated polyaniline thin film is proposed and is shown in Figure 4 (S. Saravanan et al., 2008).

Fig. 4. Tentative structure of SHI irradiated RF plasma polymerised aniline

4. Optical Studies

4.1. UV Vis NIR Studies

The photon absorption in many amorphous materials is found to obey the Tauc relation (J. Tauc, 1970), which is of the form

\[ \alpha h\nu = B (h\nu - E_{opt})^n \]  

(1)
Here $\alpha$ is the absorption coefficient, $h\nu$ the photon energy, $B$ a constant and the index $n$ is connected with the distribution of the density of states. The index $n = 1/2$ corresponds to the direct allowed transition energy gap and $n = 2$ represents the indirect allowed transition energy gap.

![Graph showing UV VIS spectra of polyaniline pristine and irradiated polyaniline at different fluences](image)

**Fig. 5.** UV VIS spectra of polyaniline pristine and irradiated polyaniline at different fluences

UV Vis absorption studies are carried out on pristine and irradiated polyaniline thin films using Hitachi U3300 spectrophotometer. The absorbance is plotted against the photon energy for polyaniline pristine and the irradiated polyaniline thin films and is depicted in Figure 5. The intercept of this plot on the photon energy axis gives the bandgap of the samples. From Figure 5, it is clear that there is a decrease in the optical bandgap of irradiated thin films. The bandgap decreases with increase of ion fluence. It can be seen that while pristine polyaniline exhibits a band gap of 3.91 eV, Polyaniline irradiated with fluence of $1 \times 10^{13}$ ions/cm$^2$ exhibits a band gap of 3.60 eV. The bombardment of swift heavy ions on these thin film samples results in rearrangement and bond shifting which leads to ring opening in which $C \equiv C$ terminals are formed. In this process the resulting product have extended conjugated structures thus reducing the band gap.

**4.2. Photoluminescence Studies**

Photoluminescence spectra were recorded for plasma polymerised aniline samples before and after irradiation and is shown in Figure 6. The pristine sample exhibits the peaks at 575nm and 680nm. After irradiation the nature of PL spectrum remains similar but the peak intensity varied with the ion fluence. The peak intensities are compared for different ion fluences. From Figure 6, it is clearly seen that the intensity of the incident beam decreases and the shoulder peak intensity increases with increase of ion fluences.
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![Graph](image1)

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![Graph](image2)

**Fig. 6.** Photoluminescence spectrum of polyaniline pristine and irradiated thin films

In general the effect of irradiation 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.
FTIR spectra indicate that the pristine polyanilene 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 increase of intensity of a shoulder peak may be attributed to the rearrangement of bonds as well as the increase of conjugation in the polymer. The incident peak intensity decreases with ion fluence. This could be due to opening of benzene rings. This is in conformity with FTIR results.

5. Electrical Studies

Capacitance and dielectric loss were measured by employing HP 4192A impedance analyser and a dielectric cell in the frequency range of 100 Hz to 1 MHz in the temperature range 300-373K. Dielectric permittivity was calculated from the known values of capacitance, thickness and the area of the sample. Further, from the measured values of dielectric constant, dielectric loss and frequency, ac conductivity was calculated by using an empirical relation

\[ \sigma_{ac} = 2\pi\varepsilon_0\varepsilon_r \tan(\delta) \]

All these measurements were made under dynamic vacuum.

5.1. Capacitance and Dielectric Loss as a Function of Frequency and Temperature

The capacitance of the plasma polymerised aniline as a function of frequency at five different temperatures is shown in Figure 7.

From Figure 7, it is found that the capacitance is frequency dependent. A circuit model proposed by Goswami and Goswami (A. Goswami, et al., 1973) explains this type of behaviour. According to the model the capacitor system is assumed to comprise a frequency independent capacitive element \( C' \) in parallel with a discrete temperature resistive element \( R \), both in series with a constant low value resistance \( r \). Basis on this model, the measured series capacitance \( C_s \) is given by

\[ C_s = C' + \frac{1}{\omega^2 R^2 C'^{1}} \]  \hspace{1cm} (2)

Dielectric loss is given by

\[ \tan(\delta) = \frac{(1 + r/R)}{\omega RC'^{1}} \]  \hspace{1cm} (3)

Where \( \omega \) is angular frequency. The temperature dependence of the model is represented by a thermally activated process and is given by

\[ R = R_0 \exp\left(-\frac{E_a}{kT}\right) \]  \hspace{1cm} (4)

Where \( R_0 \) is a constant and \( E_a \) is activation energy. Equation (2) predicts that \( C_s \) decreases with increasing \( \omega_s \) and at higher frequencies \( C_s \) remains constant for all temperatures.
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\[ C_s = \frac{C}{1 + \frac{R}{C}} \]

Dielectric loss is given by

\[ \tan \delta = \frac{C}{R} \]

Where \( \omega \) is angular frequency. The temperature dependence of the model is represented by a thermally activated process and is given by

\[ \exp \left( \frac{-E_a}{kT} \right) \]

Where \( R_0 \) is a constant and \( E_a \) is activation energy. Equation (2) predicts that \( C_s \) decreases with increasing \( \omega \) and at higher frequencies \( C_s \) remains constant for all temperatures. Equation (2) also envisages that, because of the decreasing value of \( R \), \( C_s \) will increase with increase of temperature for any frequency. This effect is shown in Figure 7 and 8.

Fig. 7. Capacitance of plasma polymerised aniline thin film as a function of frequency at different temperatures

Fig. 8. Dependence of capacitance of polyaniline thin film as a function of temperature at different frequencies
The variation of loss with frequency for different temperatures is shown in Figure 9.

![Graph showing dielectric loss as a function of frequency at different temperatures.](image)

Fig. 9. Dielectric loss of polyaniline thin film as a function of frequency at different temperatures

![Graph showing dielectric loss as a function of temperature at different frequencies.](image)

Fig. 10. Dielectric loss of polyaniline thin film as a function of temperature at different frequencies
As per equation (3) tanδ decreases with increase of frequency till the loss minimum is reached and after that tanδ increases with increase of frequency. From Figure 9, it is seen that at 373K there occurs a peak at 350Hz. It is reported that (H. Birey, 1978) similar kind of such peaks are expected at other temperatures and there occurs a peak shift. This could not be observed in our case since they might be beyond our ac measurement range. This increase of dielectric loss with decreasing frequency is usually associated with ion drift, dipole polarisation or interfacial polarisation (H. Birey, 1978). Variation of tanδ with temperature is shown in Figure 10, and is consistent with equation (3). In equation (3) the $\omega^{-1}$ term becomes dominant because of the decreasing value of R with temperature.

![Figure 9: Dielectric loss of polyaniline thin film as a function of frequency at different temperatures](image)

**Fig. 9.** Dielectric loss of polyaniline thin film as a function of frequency at different temperatures

**5.2. Dielectric permittivity as a Function of Frequency and Temperature**

The dielectric studies of plasma polymerised polyaniline thin film samples are calculated using the relation

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$  \hspace{1cm} (5)

where C is the capacitance of the sample, A is the surface area of the sample, $\varepsilon_0$ is the permittivity of air and $\varepsilon_r$ is the dielectric permittivity of the sample.

The dielectric measurement was carried out in the frequency range of 100Hz to 1MHz. The variations of dielectric permittivity with frequency for different temperatures were plotted and are shown in Figure 11. The dielectric permittivity lies in the range 7.52 and 1.38 for the entire frequency range for which the experiment was carried out (300K – 373K). The dielectric permittivity value lies between 1.45 and 1.20 at room temperature for the entire frequency range, which is considerably low. The characteristic dependence of the dielectric
permittivity can be explained with the help of interfacial polarisation mechanism. Usually, interfacial polarisation is the type of polarisation found in the sandwich configuration. The space charge accumulations at the structural interfaces of an inhomogeneous dielectric material cause the interfacial polarisation and this was explained by Maxwell and Wagner in terms of a two-layer dielectric model.

In microelectronic circuits, RC time delay can be reduced by using this type of low dielectric permittivity materials as intermetallic dielectrics (G. Maier, 2001). The time delay depends on two factors one is due to resistance of the interconnections and the other is the capacitance of the dielectric media. RC delay can be calculated by the formulae (8),

$$ RC = 2\rho k\varepsilon_0 \left[ \frac{4L^2}{P^2} + \frac{L^2}{T^2} \right] $$  (6)

where $\rho$ is the resistivity, L the length of the interconnection, T the metal thickness, $k$ the dielectric constant, $\varepsilon_0$ the permittivity of air and $P=W$ (metal Width) + $S$ (Space between metals). The dielectric permittivity of the RF plasma polymerised aniline thin film is 1.20. According to equation (6) it is found that the dielectric permittivity of polyaniline $k=1.20$ will reduce RC delay by about 70%.

### 5.3. AC Conductivity as a Function of Frequency and Temperature

The variation of ac conductivity $\sigma_{ac}$ as a function of frequency for different temperatures of RF plasma polymerised aniline thin film is shown in Figure 12. From Figure 12, it is seen that the conductivity increases with increase in temperature and frequency. The conductivity increases rapidly at higher frequencies.

Fig. 12. Ac conductivity of polyaniline thin film as a function of frequency at different temperatures
This can be interpreted by involving the following empirical relation (N. F. Mott et al., 1971)

\[ \sigma(\omega) \propto \omega^n \]  
(7)

where \(\omega\) is the angular frequency and \(n\) is the index used to understand the type of conduction mechanism in amorphous materials.

The values of \(n\) determined from Figure 12. lie between 0.5 and 1.1 for lower frequencies. The value of \(n\) in this frequency range is in accordance with the theory of hopping conduction in amorphous materials (M. Pollock, 1961).

The value of \(n\) gives the type of the dominant conduction mechanism in amorphous materials. This power law is an approximation of the Austin and Mott model, which describes the ac conductivity. Phonon assisted hopping of charge carriers through tunnelling from a localised site to another one is the basic physics behind the power law relation predicted by the Austin and Mott (A. N. Papathanassiou, 2002). Also Mott and Austin explained the dependence of ac conductivity at lower temperatures by the relation (A. N. Papathanassiou, 2002)

\[ \sigma_{ac} = A \left( \frac{e^2}{\alpha} \right) \left\{ N(E_F) \right\}^2 kT \omega \left\{ \ln \left( \frac{v_{ph}}{\omega} \right) \right\}^4 \]  
(8)

This relation can be modified as follows by differentiating with respect to \(\omega\)

\[ \frac{d \ln \sigma_{ac}(\omega)}{d \ln \omega} = 1 - \frac{4}{\ln \left( \frac{v_{ph}}{\omega} \right)} \]  
(9)

The value of \(n\) also determined by the phonon frequency and it depends on the ac frequency (A. N. Papathanassiou, 2002).

Figure 13. is the plot between \(d\log \sigma_{ac}/d\log \omega\) and log frequency for three typical values of the parameter \(v_{ph}: 10^{12}, 10^{13}, 10^{14}\) Hz. From the Figure 13. it is seen that, depending on the phonon frequency the value of \(d\log \sigma_{ac}/d\log \omega\) lies between 0.71 - 0.88 for the entire frequency range. The predicted values of \(n\) lie within the values of \(n\) obtained from our experiments, provided that a single hopping ac conductivity mechanism operates in the plasma polymerised aniline thin films. Based on this it may be concluded that the conductivity is due to hopping. Also it is necessary to compare the experimental and the predicted values for finding out whether it is single or multiple hopping conductivity (A. N. Papathanassiou, 2002).
The variation of ac conductivity with temperature as a function of different frequencies is shown in Figure 14. Activation energies were calculated and are found to be in the range 0.356 eV - 0.1435 eV, which is considerably low. From Figure 14, it is seen that the ac conductivity of the RF plasma polymerised polyaniline thin films is frequency dependent and it has very low activation energy. The low activation energies of these films indicate that hopping conduction mechanism occurs in RF plasma polymerised aniline thin films.
5.4. Effect of Swift Heavy Ions on Dielectric Permittivity

The dielectric measurements were performed on the irradiated polyaniline thin films and pristine polyaniline films and are shown in Figure 15. The dielectric permittivity for pristine films decreases with increase of frequency. The value of dielectric permittivity for the irradiated thin films is less than one. This violates the classical mechanical rule. It is also observed that the dielectric permittivity decreases with increase of ion fluence. This decrease in the dielectric permittivity can be explained on the basis of the decrease in the number of sites, which are available for polarization and flow of space charge carriers, which could be correlated to the production of defects created in the thin films due to the irradiation.

![Dielectric Permittivity Graph](image)

**Fig. 15. Variation of Dielectric permittivity with ion Fluences**

It may be noted here that irradiated samples exhibit ultra low dielectric permittivity (k<1). There is no immediate explanation for this observation and further investigations are necessary to ascertain the origin of ultra low permittivity in swift heavy ion irradiated thin films. In literature reports on ultra low are scanty. (R. I Mohamed, 2000)

6. Conclusion

RF plasma polymerised aniline thin films were prepared and irradiated with swift heavy ions. The effect of SHI on the structural, optical and electrical properties was studied. FTIR spectral results were compared with the standard data and based on the analysis a tentative structure for the pristine polyaniline and the irradiated polyaniline were proposed. The change in optical band gaps for irradiated samples was evaluated and found that the optical band gap reduces with increase of ion fluence. Electrical studies were carried out on the irradiated thin films and the results were compared with the pristine thin films.
7. Acknowledgments

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8. References


This book provides a timely overview of a current state of knowledge of the use of polymer thin film for important technological applications. Polymer thin film book covers the scientific principles and technologies that are necessary to implement the use of polymer electronic device. A wide-ranging and definitive coverage of this emerging field is provided for both academic and practicing scientists. The book is intended to enable readers with a specific background, e.g. polymer nanotechnology, to become acquainted with other specialist aspects of this multidisciplinary field. Part A of the book covers the fundamental of the key aspect related to the development and improvement of polymer thin film technology and part B covers more advanced aspects of the technology are dealt with nano-polymer layer which provide an up-to-date survey of current research directions in the area of polymer thin film and its application skills.

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