CHAPTER 3

Plasma Polymerized Aniline

Since the discovery of organic semiconductors in 1977 [1], knowledge in this field has grown significantly. Polyaniline is one prominent class of such materials due to the interesting electronic and optical properties [2–6]. Recent years have shown growing interest in the preparation of plasma polymerized aniline (PPA) films due to the new challenges of their use as optoelectronic materials [7–9]. The goal is to achieve materials with specified set of electrical and optoelectronic properties for the manufacture of luminescent and photosensitive transport layers of uniform and homogeneous thickness and to be used as nonlinear optical materials. The optical absorption in pristine polyaniline due to $\pi-\pi^*$ transition is very sensitive to the change in the environment around the phenyl ring [4]. Moreover, the chain structure exerts a considerable effect on the nature and radiative properties of excited states in $\pi$-conjugated system. Chemical reactions that occur under plasma conditions are generally very complex and non-specific in nature. Glow discharge polymerization of organic compounds seems to proceed via free radical mechanism and the extent of ionization is small [7–9]. The reaction mechanisms are very different from those of classical chemical processes and precursor molecules are continuously and randomly fragmented before they recombine [7–11].

Aniline belongs to aromatic monomers which in the plasma phase might produce mono-radical and bi-radical species initiating the propagation of the polymerization. Mono-radical species can be formed by detachment of hydrogen atoms from the amino group or aromatic ring and by detachment of the amino group from the aromatic ring. Bi-radical species can be formed by aromatic ring opening, and π-bond scission. The polymer-like PPA resulting from plasma polymerization usually does not contain regularly repeating units; the chains are branched and are randomly terminated with high degree of cross-linking. In most cases a number of free radicals which cannot recombine rapidly are trapped in the growing film which changes the network over time.

![Graph](image)

**Figure 3.1:** Electron temperature ($T_e$) of aniline plasma and deposition rate of PPA. $T_e$ and deposition rate increases with input RF power. $T_e$ is higher at lower pressure ($p_{aniline} = 0.06$ mbar) but the deposition rate is significantly lower at lower pressure.

### 3.1 Plasma Conditions for PPA depositions

In low temperature aniline RF plasma, electrons and vacuum ultraviolet (VUV) photons are the primary oxidizing agents. Moreover, in low pressure low temperature non-equilibrium discharges, energetic electrons and VUV photons induce ionization,
excitation and molecular fragmentation processes leading to a complex mixture of active species that undergo recombination processes in the presence or absence of plasma [7,12]. Figure 3.1 shows the variation of electron temperature of aniline plasma and deposition rate of PPA vs input RF power at different working pressure. The electron temperature and deposition rate increase with input power for both at 0.06 and 0.15 mbar. The degree of fragmentation, excitation, and ionization of monomer molecules depends on the energy of the electrons. It has been observed that $T_e$ is higher at 0.06 mbar, but the deposition rate is significantly lower at lower pressure. Lower electron temperature and higher deposition rate at higher working pressure favour the retention of the monomer structure. Plasma electrons having higher velocities of thermal motion can play the determining role in the polymerization initiation processes. The energetic electrons of plasma are responsible for the dissociation of chemical bonds involved in the organic structure. Debarnot et al [7] reported that PPA films deposited at low $W/FM$ ($W$, input power; $F$, flow rate; $M$, precursor molecular weight) value retains more of the monomer structure. At higher working pressure and low power, the $W/FM$ parameter is low and the plasma is energy deficient. The fragmentation of the precursor is low leading to high retention of the monomer structure. On the contrary, at high values of $W/FM$, the plasma is monomer deficient inducing the scission of almost all precursor bonds.

3.2 Structure and Morphology

Figure 3.2 depicts FTIR transmittance spectra of PPA deposited at different plasma conditions. PPA present most of the characteristic bands of linear polyaniline. At a lower (Ar+aniline) pressure, the bands at 1498 and 1601 cm$^{-1}$ are assigned to C=C stretch of benzenoid and quinoid units, respectively [4]. The strong absorption at 1040 cm$^{-1}$ may be due to in-plane C–H deformation [13]. The band at 3330 cm$^{-1}$ is assigned to secondary amine N–H stretch and the bands in the range 3448–3855 cm$^{-1}$ are due to OH stretch of adsorbed water. However, FTIR spectra present more intense unsaturated bands for films deposited without Ar assistance and at a higher working pressure. At higher pressure, PPA exhibit retention of aromaticity confirmed by the presence of intense bands at 1498 and 1601 cm$^{-1}$ due to aromatic units.
Figure 3.2: FTIR transmittance spectra of PPA film deposited at (a) $P_{\text{RF}} = 20$ W, $P_{\text{Ar+aniline}} = 0.06$ mbar, (inset) without Ar as carrier gas, (b) $p_{\text{aniline}} = 0.15$ mbar, $P_{\text{RF}} = 20$–50 W. (c) FTIR spectra of PPA film and powder at $p_{\text{aniline}} = 0.15$ mbar, $P_{\text{RF}} = 20$ W, $t_T = 65$ min, (d) FTIR spectra of PPA for different polymerization time at $p_{\text{aniline}} = 0.15$ mbar, $P_{\text{RF}} = 20$ W, (e) bands area ratio $(\text{C–H})_{\text{sat}}/(\text{C–H})_{\text{unsat}}$ vs polymerization time.
Moreover, the retention of aromaticity is confirmed for all polymerization time in 10–65 min range. However, the appearance of band at 2931 cm\(^{-1}\), which is assigned to saturated C–H stretch, indicates the partial loss of aromaticity during plasma polymerization. Figure 3.2c shows the FTIR transmittance spectra of PPA of 65 min polymerization time in film mode as well as for powder collected from the excitation electrode. The important aspect is the evolution of intense band at 1385 cm\(^{-1}\) in powder form which is assigned to C–N stretching band. Surprisingly, this band is not at all observable in the film mode. The intensity of this band corresponds to polymer chain length increase. This band is treated as diagnostic of chain length [14] and the enhancement of its intensity dictates the continuous conjugation of polymer chain leading to exposure of hidden C–N groups in powder form. The band assignments are summarized in Table 3.1. Thanks to the evolution of a band at 1313 cm\(^{-1}\), in both film and powder form, which is again assigned to C–N stretch, indicating extended conjugation in both film and powder mode. The bands at 696 and 752 cm\(^{-1}\) suggest crosslinking in PPA. The weak intensity band at 835 cm\(^{-1}\) compared with 696 and 752 cm\(^{-1}\) is an indication of branched and crosslinked polymer-like structure [9]. Figure 3.2e shows the ratio of bands area of saturated C–H stretch to unsaturated (aromatic and alkenes) C–H stretch vs reaction time. The ratio is less than unity till reaction time increases to 20 min and then increases with reaction time. This suggests ring opening is prominent with increase in polymerization time. Further, weak absorption band at 2212 cm\(^{-1}\) is due to the C≡N stretch of nitrile group leading to possible chain termination under the plasma environment. From the FTIR spectra, it is clear that PPA cannot be in leucoemeraldine base (LB) form as the latter exhibits a very low intensity ratio of 1601 to 1498 cm\(^{-1}\). Also, LB does not absorb at 1385 cm\(^{-1}\) while emeraldine base (EB) does [4]. EB has about equal intensities for 1601 and 1498 cm\(^{-1}\) peak. On the other hand, 75% intrinsically oxidized nigraniline base (NB) and fully oxidized pemigraniline base (PNB) show an enhanced quinoid to benzenoid intensity ratio. Hence, owing to the high intensity ratio of quinoid to benzenoid units, in most cases, PPA are in higher oxidation state, but at the same time cannot be approximated to NB or PNB form as the PPA have different optical absorption spectra as compared with NB or PNB and so represents a unique polymer-like structure. The energy of electrons in cold RF plasma is sufficient to
dissociate almost all chemical bonds involved in the organic structure. But at the same time, higher energies are usually required for the dissociation of unsaturated bonds and the formation of multiple free radicals. Accordingly, initial or plasma generated unsaturated linkages will have a better survival rate under plasma conditions compared with the \(\sigma\)-linkages \[12\]. Therefore, PPA is characterized by unsaturated, branched, and crosslinked architecture.

**Table 3.1**: Assignments of IR absorption bands of PPA.

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3379–3365</td>
<td>Secondary amine N–H stretch</td>
</tr>
<tr>
<td>3052–3028</td>
<td>Unsaturated (aromatic and alkenes) C–H stretch</td>
</tr>
<tr>
<td>2949–2921</td>
<td>Saturated C–H stretch</td>
</tr>
<tr>
<td>2212</td>
<td>C=\text{N} stretch of nitrile group</td>
</tr>
<tr>
<td>1601</td>
<td>C=\text{C} stretch of quinoid unit</td>
</tr>
<tr>
<td>1498</td>
<td>C=\text{C} stretch of benzenoid unit</td>
</tr>
<tr>
<td>1385</td>
<td>C–N stretch of QBQ</td>
</tr>
<tr>
<td>1313–1308</td>
<td>C–N stretch (QBQ, QBB, BBQ)</td>
</tr>
<tr>
<td>835</td>
<td>1, 4 di-substituted aromatic ring (para)</td>
</tr>
<tr>
<td>752</td>
<td>1, 2 di-substituted aromatic ring (ortho)</td>
</tr>
<tr>
<td>696</td>
<td>1, 3 di-substituted aromatic ring (meta)</td>
</tr>
</tbody>
</table>

\(\text{Q, quinoid unit; B, benzenoid unit}\)

Figure 3.3 shows the wide angle x-ray diffraction (WAXD) pattern of PPA. The characteristic broadening of x-ray diffraction peak at 20 \(\approx\)18.5° implies amorphous nature of PPA. Also, the deposition parameters have no significant effect on the WAXD pattern of PPA. PPA possess a rather disordered structure. Figure 3.4 shows AFM image of PPA film of 65 min polymerization time. The RMS surface roughness, \(R_q\) are 4.9, 3.2, and 2.1 nm, respectively for films deposited with 15, 30, and 65 min polymerization time. The values of \(R_q\) decrease with polymerization time. With increase of polymerization time uniform, dense and smooth surfaces are obtained.
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Figure 3.3: Wide angle X-ray diffraction pattern of PPA powder. $P_{RF} = 20$ W, $P_{aniline} = 0.15$ mbar. Reaction time has no significant effect on WAXD pattern.

Figure 3.4: AFM scan image (2.0 $\times$ 2.0 $\mu$m$^2$ area) of PPA film deposited for 65 min polymerization time. The rms value of roughness is also noted.
Figure 3.5: UV-VIS-NIR transmittance spectra of PPA films deposited on quartz substrate at (a) $p_{\text{aniline}} = 0.06$ mbar, $t_r = 65$ min, and $P_{\text{RF}} = 10-30$ W, (b) $p_{\text{aniline}} = 0.15$ mbar, $t_r = 30$ min, and $P_{\text{RF}} = 20-50$ W, (c) $P_{\text{RF}} = 20$ W, $t_r = 65$ min, $p_{\text{aniline}} = 0.06$ and 0.15 mbar, (d) $p_{\text{aniline}} = 0.15$ mbar, $P_{\text{RF}} = 20$ W, and $t_r = 10-65$ min. The dotted black curve is the transmittance spectrum of quartz substrate. Transmittance edges are red shifted with increasing $P_{\text{RF}}, p_{\text{aniline}}$, and $t_r$. 

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3.3 Optoelectronic Properties

The spectral dependence of transmittance for PPA films is shown in Figure 3.5. PPA films are highly transparent in the near-IR region; the film deposited with $P_{RF} = 20$ W, $p_{aniline} = 0.15$ mbar, and $t = 65$ min has transmittance close to the transmittance of quartz substrate at and above 1120 nm and hence these films could be promising candidates for IR optics applications. The absorbance edge shows systematic red shift with increase of $P_{RF}$, $P_{aniline}$, and $t$. Also, PPA exhibit broad absorbance band in the UV and visible region. The red shift and wide absorbance band with input power, working pressure, and polymerization time might be due to increased cross-linking density. Moreover, none of the characteristic peaks of EB (330, 630 nm), LB (343 nm) and PNB (283, 327 nm) is distinguishable, the optical absorbance provides further evidence of the differences in the structure of PPA films when compared with chemically or electrochemically synthesized polyaniline. The position of the absorbance band of pristine polyaniline is dependent on chain length as well as on the distribution of benzenoid and quinoid rings [4]. The broad absorbance in the UV and visible region makes PPA films useful for photovoltaic applications. Efforts have been devoted for broad absorption spectra and to enhance charge carrier mobility of conjugated polymer photovoltaic materials [15]. This is mostly achieved by crosslinking of the polymer main chain with conjugated bridges. The optical band gap $E_g$ can be determined from the absorption coefficient, $\alpha$ calculated as a function of incident photon energy, $h\nu$, and is expressed by the Tauc relation [16]:

$$\alpha h \nu = B (h \nu - E_g)^m$$

(3.1)

Here $B$ is energy independent constant. The optical transitions in semiconductors are characterized by $m$ values, $1/2$ for allowed direct, 2 for allowed indirect, 3 for forbidden direct, and 3/2 for forbidden indirect [17]. The fundamental absorption edge in PPA is characterized by direct allowed transition where $m = 1/2$. The value of $m$ can be determined by the procedure described by Yakuphanoglu et al. [18]. Figure 3.6 shows representative Tauc plot of PPA. The optical band gaps are obtained from the extrapolation of the linear part of the plot $(\alpha h \nu)^2$ vs $h\nu$ at $(\alpha h \nu)^2 = 0$. The optical band gap decreases from 2.95 to 2.28 eV with polymerization time.
The increase in cross-linking density favours reduction of optical band gap with increase of $P_{RF}$, $p_{aniline}$, and $t_r$. In organic semiconductor, the energy of separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is known as the fundamental HOMO-LUMO gap $E_{gl}$, which is the minimum energy of formation of a separated, uncorrelated electron and hole [19]. The optical band gap $E_g$ corresponds to the onset of optical absorption and formation of exciton. Because of strong localization of carriers in conjugated polymers compared with inorganic semiconductors, the binding energy of exciton, $E_b$ is significantly higher. The consensus from experimental results is $E_b = 0.5-1.0$ eV in organic semiconductors [20]. So, $E_{gl}$ is larger than $E_g$ by significant amount.

The knowledge of values of wavelength dependent optical constants of thin solid films is very important, both from fundamental and technological viewpoint. For PPA, it is important to know the spectral dependence of refractive index, $n$ and extinction coefficient, $k$ to predict its optoelectronic behaviour. The values of $n$ and $k$ in the near-IR region have been extracted for PPA films deposited under different deposition conditions by using the Swanepoel technique [21].
Figure 3.7: (a–c) Refractive indices of PPA films. (d–f) Extinction coefficients of PPA films. Dense and smooth structures are obtained at higher working pressure and longer reaction time. However, at $p_{\text{amine}} = 0.15$ mbar and $P_{\text{RF}} = 50$ W, PPA exhibits less dense structure than PPA deposited at $P_{\text{RF}} = 30$ W.
In the Swanepoel method, the refractive index of the substrate is given by

\[ s = \frac{1}{T_s} + \sqrt{\frac{1}{T_s^2} - 1} \]  

(3.2)

where \( T_s \) is the transmittance of the substrate. In the region of weak and medium absorption, the refractive index of PPA

\[ n_1 = \sqrt{(N + \sqrt{N^2 - s^2})} \]  

(3.3)

where \( N = 2s\frac{T_M - T_m}{T_m T_M} + \frac{s^2 + 1}{2} \) and \( T_M \) and \( T_m \) are the transmittance maximum and minimum of interference fringes obtained by making smooth envelopes. The basic equation for interference fringes

\[ 2nd = m\lambda \]  

(3.4)

where \( d \) is the thickness of the film, \( m \) is integer for maxima and half integer for minima. For two adjacent maxima (or minima) at \( \lambda_1 \) and \( \lambda_2 \)

\[ d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \]  

(3.5)

The average value of \( d \) together with \( n_1 \) now can be used to determine \( m \). By proper selection of \( m \), the final \( d \) and \( n \) can be calculated using the Eq. 3.4. The extinction coefficient \( k \) can be determined from the absorption coefficient \( \alpha \),

\[ k = \frac{\alpha \lambda}{4\pi} \]  

(3.6)

where \( \alpha(\lambda) \) can be determined by using equations given at the appendix A. The plots of the refractive indices \( n \) and extinction coefficients \( k \) vs wavelength are shown in Figure 3.7. The optical constants \( n \) and \( k \) directly relate to the structure and composition of the material. As the polymerization time or working pressure increases the refractive index increases. This suggests that films have more dense structure; the higher reaction time
and working pressure are contributing to the higher values of refractive index. The loss of light in PPA results from absorption and scattering. The film with 65 min polymerization time has very low values of $k$ in the infrared. With low polymerization time, higher $k$ values suggest scattering loss due to surface imperfections such as roughness and also due to the lower levels of transmission. The result is consistent with the AFM observation as more dense and smooth structure is formed at longer reaction time. Moreover, for $\lambda \leq 1064$ nm, the lowest value of $n$ is comfortably above the required minimum of 1.5 for waveguide applications [22].

Information of non-linear optical parameters of conjugated polymers is important for their potential application in non-linear optical devices. The dispersion relationship can be quite complicated in practice. Below interband absorption edge the dispersion relation is given by the Wemple-DiDomenico single oscillator model [23]

$$n^2 = 1 + \frac{E_d E_0}{E_0^2 - (h\nu)^2}$$

(3.7)

where $E_d$ is the dispersion energy, a measure of the strength of interband optical transitions, $E_0$ is the single oscillator energy which reflects overall band structure information. The plot of $(n^2 - 1)^{-1}$ vs $(h\nu)^2$ is shown in Figure 3.8a. From the slope and intercept, $E_0$ and $E_d$ can be determined. At long wavelengths, a positive curvature deviation from linearity is usually observed due to the negative contribution of lattice vibrations to the refractive index. The relation between the refractive index, $n$ and lattice dielectric constant $\varepsilon_L$ is given by [24]

$$n^2 = \varepsilon_L - B\lambda^2$$

(3.8)

where $B = \frac{e^2 N}{4\pi^2 c^2 \varepsilon_0 m^*}$ is a constant. Here $N$, $e$, $\varepsilon_0$, $c$ and $m^*$ are free charge carrier concentration, electronic charge, permittivity of free space, speed of light in vacuum and effective mass of charge carrier, respectively. The extrapolation of the linear part of the plot $n^2$ vs $\lambda^2$ (Figure 3.8b) at $\lambda^2 = 0$ gives the value of $\varepsilon_L$. The value of $N/m^*$ is
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determined from the slope of the linear part. In the long wavelength approximation, the single term Sellmeier relation [25]

\[ n^2 - 1 = \frac{S_0 \lambda_0^2}{1 - \frac{\lambda_0^2}{\lambda^2}} \]  

(3.9)

where \( \lambda_0 \) is the average oscillator wavelength and \( S_0 \) is the average oscillator strength. The parameters \( S_0 \) and \( \lambda_0 \) can be obtained from the plot \((n^2 - 1)^{-1} vs \lambda^2\). This is shown in Figure 3.8c. In the range of transparency when the electron damping parameter, \( \gamma < \omega \), the refractive index is related to the plasma frequency \( \omega_p \) by the relation [17]

\[ n^2 = \epsilon_0 \left( \frac{\omega_p^2}{\omega^2} \right) \]  

(3.10)

Hence \( \omega_p \) can be estimated. The estimated values of the dispersion parameters of PPA are recorded in Table 3.2, where dielectric constants \( \epsilon_1 \) and \( \epsilon_2 \) are calculated by using the relation [17]

\[ \epsilon_1 = n^2 - k^2, \epsilon_2 = 2nk \]  

(3.11)

The values of \( n \) and \( k \) are used for \( \lambda = 1064 \) nm, typical wavelength of Nd:YAG laser. Higher binding energy of excitons in PPA is a direct consequence of low dielectric constant, \( \epsilon_1 < 4 \).

Figure 3.8: Dispersion plots of PPA films deposited at \( P_{RF} = 20 \) W, \( P_{aniline} = 0.15 \) mbar, and \( t_r = 65 \) min, (a) \((n^2 - 1)^{-1} vs (hv)^2\), (b) \( n^2 vs \lambda^2 \), (c) \((n^2 - 1)^{-1} vs \lambda^{-2}\).
Table 3.2: Dispersion parameters of PPA.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Reaction time (min)</th>
<th>Pressure (mbar)</th>
<th>RF power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{RF}$, 20 W; $p_{aniline}$, 0.15 mbar</td>
<td>$P_{RF}$, 20 W; $t_r$, 65 min</td>
<td>$p_{aniline}$, 0.15 mbar; $t_r$, 30 min</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>65</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.06</td>
<td>50</td>
</tr>
<tr>
<td>$n$</td>
<td>1.55</td>
<td>1.74</td>
<td>1.65</td>
</tr>
<tr>
<td>$k$</td>
<td>1.04×10^{-3}</td>
<td>1.29×10^{-4}</td>
<td>8.49×10^{-4}</td>
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<tr>
<td>$\varepsilon_1$</td>
<td>2.40</td>
<td>3.03</td>
<td>2.72</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>3.95×10^{-3}</td>
<td>4.50×10^{-4}</td>
<td>9.5×10^{-3}</td>
</tr>
<tr>
<td>$E_0$ (eV)</td>
<td>5.24</td>
<td>5.36</td>
<td>6.99</td>
</tr>
<tr>
<td>$E_d$ (eV)</td>
<td>6.92</td>
<td>10.32</td>
<td>11.71</td>
</tr>
<tr>
<td>$\varepsilon_L$</td>
<td>2.45</td>
<td>3.09</td>
<td>2.74</td>
</tr>
<tr>
<td>$S_0$ ($\times10^{13}$ m^{-2})</td>
<td>1.91</td>
<td>3.23</td>
<td>5.33</td>
</tr>
<tr>
<td>$\lambda_0$ (nm)</td>
<td>260.96</td>
<td>243.39</td>
<td>177.21</td>
</tr>
<tr>
<td>$N/m^*$ (m^{-3} kg^{-1})</td>
<td>5.84×10^{55}</td>
<td>6.89×10^{55}</td>
<td>2.06×10^{55}</td>
</tr>
<tr>
<td>$\omega_p$ (Hz)</td>
<td>4.11×10^{14}</td>
<td>4.46×10^{14}</td>
<td>5.88×10^{14}</td>
</tr>
</tbody>
</table>

($n$, refractive index; $k$, extinction coefficient; $\varepsilon_1$, real part of dielectric constant; $\varepsilon_2$, imaginary part of dielectric constant; $\varepsilon_L$, lattice dielectric constant; $E_0$, single oscillator energy; $E_d$, dispersion energy; $\omega_p$, plasma frequency; $N$, free charge carrier concentration; $m^*$, effective mass of charge carrier; $\lambda_0$, average oscillator wavelength; $S_0$, average oscillator strength)

Processing of conjugated polymer films with high conjugation lengths through a reduction of the competing non-radiative decay processes is one of the possible strategies for light emitting diode and photodiode applications. The structure of plasma produced polymer-like films critically depends on the processing condition. Figure 3.9a shows the photoluminescence spectra of PPA films. The PL peak at ~650 nm is observed upon excitation with 390 nm. The excitation wavelengths are set at 390 and 65 nm.
490 nm as they fall inside the broad absorbance band of the films under investigation. Shimano et al. [26] reported the emission of light in chemically synthesized polyaniline films of EB and LB states, where the luminescence is caused by the reduced amine (benzenoid) groups and is quenched by the adjacent oxidized imine (quinoid) groups. In the inset, FTIR absorption bands area ratio of quinoid (1601 cm\(^{-1}\)) to benzenoid (1498 cm\(^{-1}\)) is shown which implies that the higher the ratio of quinoid to benzenoid, lower is the photoluminescence. As shown in Figure 3.9b, the PL peak at 650 nm is slightly red shifted to 679 nm when excitation wavelength is changed to 490 nm. Because of the strong localization of carriers, the exciton within molecule and charge transfer exciton could be responsible for the PL in PPA films. The excitons generated with the photo-excitation relax to sites of lower energy to maintain a dynamic equilibrium via radiative (luminescence) or non-radiative decay channels. Macroscopic exciton delocalization is usually possible for structurally perfect polymer chain [27]. However, for PPA, conjugation is usually not maintained along the entire backbone, it rather extends over a segment of the chain only. The limitation of conjugation is a consequence of kinks, cross-links, defects and torsion around some bonds. These could restrict the conjugation along the entire backbone, rather extends over a segment only called spectroscopic units [27] which may give rise to PL features.

Figure 3.9: (a) Photoluminescence spectra of PPA films deposited for \(t_r = 20, 30,\) and 65 min at \(P_{RF} = 20\) W and \(p_{aniline} = 0.15\) mbar. In the inset the FTIR absorption bands area ratio of quinoid to benzenoid is shown. Excitation wavelength is 390 nm, (b) PL spectra of PPA film with \(t_r\) of 30 min.
Figure 3.10: Thermo-gravimetric analysis in air of PPA powder of different polymerization time. In the inset the coupled DSC-TGA curves of PPA of 65 min polymerization time in argon atmosphere. Here $P_{RF}$, 20 W; $p_{aniline}$, 0.15 mbar.

3.4 Thermal Stability

Plasma polymerized aniline exhibits thermal stability. Figure 3.10 shows the thermogravimetric analysis (TGA) of PPA carried out in air and argon atmosphere. The first weight loss (2% at 393 K) occurs due to the moisture evaporation. The second weight loss occurs in the region 400–770 K, may be attributed to the weight loss due to degradation of aliphatic units as PPA contains both aromatic and aliphatic units [28]. The final and major weight loss occurs in the region 800–1070 K due to structural decomposition. The coupled TGA-DSC curve in argon atmosphere is shown in the inset in Figure 3.10 for PPA of 65 min polymerization time. Under argon atmosphere, 46.8% weight remains at 1073 K which indicates that PPA is much more stable in argon atmosphere than in air. As DSC measures the total heat flow and sum of all transitions in the sample, the glass transition temperature may be masked by the endothermic reactions of moisture evaporation and exothermic crosslinking peak (~418 K). So, the glass transition temperature is difficult to identify by conventional DSC. The exothermic peak at ~788 K is due to the degradation of polymer at this temperature. Moreover, PPA undergo equal weight loss in air and inert atmosphere till temperature
reaches up to 800 K. Higher onset decomposition temperature is enough for optoelectronic applications.

3.5 Summary

The structural study reveals that plasma polymerized aniline (PPA) has extended conjugation and higher oxidation levels in most cases. In its powder form, PPA has enhanced chain length confirmed by the evolution of C–N stretching band at 1385 cm$^{-1}$. The material is structurally different from the chemically synthesized polyaniline and none of the characteristic peaks of polyaniline is observable in the optical absorbance spectra and hence represents a unique polymer-like structure. At a higher working pressure, the deposition rate is drastically higher and electron energy is low which suggests less dissociation of chemical bonds involved in PPA structure. The transmittance edges exhibit systematic red shift with increasing the reaction time, working pressure, and input power. The broad absorbance band in the ultraviolet and visible region and optical band gap falling in the semiconducting region for these films suggest the materials to be useful for photovoltaic applications. The high degree of crosslinking of conjugated chains causes the red shift of the absorption spectrum and with proper optimization, ordered networks with high conjugation lengths could be achieved in plasma polymerized aniline films for sustaining as optoelectronic material for light emitting diode and photodiode applications. Surface roughness is reduced and dense structure is formed with higher working pressure and longer reaction time. The optical dispersion study using the Wemple-DiDomenico single oscillator model and the single term Sellmeier relation provides useful information on dispersion parameters of RF plasma polymerized aniline films which are crucial in the design and development of nonlinear optical components. The occurrence of photoluminescence peaks could be attributed to the presence of benzenoid units where the PL is quenched by the adjacent quinoid units. The glass transition temperature is masked by the endothermic reactions of moisture evaporation and exothermic crosslinking reactions. The higher onset decomposition temperature and similar thermal stability in air and inert atmosphere till 770 K is enough for needed stability for optoelectronic applications. The study reveals
that plasma polymerization is a versatile technique for PPA depositions where the process parameters could play crucial role in the band gap engineering of the material. It may be concluded that plasma polymerized aniline is an optically promising material.

3.6 References


