Chapter 5

Results and Discussion

5.1 Introduction:

This chapter elaborates the significant results obtained through the characterization of polymer polyaniline (PANI) synthesized by using oxidative and emulsion polymerization process. The detailed experimental procedure of both the synthesis processes is explained in chapter 4. In present work, all the PANI thin films were prepared by using spin coating method. The deposited thin films of PANI were characterized by using, UV-Visible spectroscopy, FTIR spectroscopy, Scanning Electron Microscopy (SEM), Nuclear Magnetic Resonance (H-NMR). The nano-particle sizes of PANI were confirmed by Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD). The conductivity of PANI films was measured by four probe method. The Refractive Index (R.I.) and thickness measurement of the deposited films were conducted with the help of ellipsometry characterization. The ohmic behavior of the prepared films was determined by current-voltage (I-V) analyzer. The mechanism of interaction between PANI and ammonia has been explained in detail. Further, the sensing ability of the prepared PANI thin films was investigated at different concentrations of ammonia (ranging from 50 ppm to 1000 ppm).

5.2 UV-Visible Analysis of PANI:

The UV –Visible absorption spectrum of the synthesized PANI by oxidative polymerization and emulsion polymerization at room temperature is shown in Fig. 5.1(a) and Fig. 5.1(b) respectively. The UV spectra of PANI were measured on Chemto Spectra Scan V2700. The conductive behavior of PANI is related to electronic transitions which takes place in the visible spectrum. The IR spectrum allows the determination of the relative amounts of the quinonoid and benzenoid moieties in the PANI chains; the conductive PANI has equal amounts of both types [1]. The peak at 300 nm and 320 nm corresponds to the n- n* transition of the benzenoid ring, while the sharp trough at 430
nm and 440 nm can be assigned to the localized polaron (i.e., excitonic transition of quinoid rings) which are characteristics of the protonated PANI, obtained by oxidative and emulsion polymerization respectively. The broad peak at 660 nm and 620 nm is related to the doping level and the formation of polarons of the conducting form together with extended tail nearly at 800 nm and 740 nm representing the conducting ES (Emeraldine Salt) state of PANI, synthesized through oxidative and emulsion polymerization respectively. This confirms the formation of PANI [2-3].

Figure 5.1(a): UV-Visible Absorption Spectrum of PANI (Oxidative polymerization)

Figure 5.1(b): UV-Visible Absorption Spectrum of PANI (Emulsion polymerization)
5.3 Characterization of spin coated PANI films:

The present investigations relates to response of PANI films prepared by spin coating method. The prepared thin films of PANI were characterized by various characterization techniques. The FTIR and UV-Vis spectral studies indicate that PANI sample exist primarily as polysemiquinone radical cations. Further the prepared films were used for detection of ammonia at different concentrations (from 50 ppm to 1000 ppm).

5.4 Fourier Transform Infrared spectroscopy analysis:

5.4.1 FTIR analysis of PANI thin film: (Oxidative polymerization)

![Figure 5.2(a): FTIR spectra of PANI film](image)

The FTIR spectrum of PANI thin film is shown in Fig. 5.2(a). The polymer material PANI required to prepare the film was synthesized by oxidative polymerization. This study is useful to determine the chain orientation, structure of polymer and also used to elucidate mechanism of polymerization. The FTIR analysis was done by Nicolet 380 spectrophotometer in our laboratory. The IR spectrum shows N-H stretching vibration band at 3557 cm\(^{-1}\) and at 2945 cm\(^{-1}\). The characteristic band appeared at 1583 cm\(^{-1}\) indicates nitrogen bond between benzoid and quinoid rings respectively. The band at
1668 cm\(^{-1}\) corresponds to C=C stretching (phenyl ring). The peak at 1305 cm\(^{-1}\) is assigned to C-N stretching of tertiary aromatic amine. The peak at 815 cm\(^{-1}\) is due to an aromatic \(=C-H\) plane bending. This shows very good agreement with results reported by P. R. Hota and group [4].

5.4.2 FTIR spectral studies of film of PANI: (Emulsion polymerization)

The FTIR spectral studies of PANI film are demonstrated in Fig. 5.2(b). The nanoparticles of PANI were obtained by the synthesis process ‘emulsion polymerization’. Further the films were prepared by using spin coating method. During polymerization, the temperature was kept constant nearly at 16°C but the mechanical stirring rate of reaction solution was maintain at different rpm i.e. 200, 400 and 600 rpm. The IR spectrum shows N-H stretching vibration band at 2947 cm\(^{-1}\), 2980 cm\(^{-1}\) and 2983 cm\(^{-1}\) respectively for 200, 400 and 600 rpm [5].

![FTIR spectra of nanoparticles of polyaniline (at solution stirring rate 200, 400, 600 rpm)](image)

Figure 5.2 (b): FTIR spectra of nanoparticles of polyaniline (at solution stirring rate 200, 400, 600 rpm)

The characteristic band appeared at 1585 cm\(^{-1}\), 1451 cm\(^{-1}\), 1560 cm\(^{-1}\) and 1465 cm\(^{-1}\), 1559 cm\(^{-1}\), 1453 cm\(^{-1}\) indicates nitrogen bond between benzenoid and quinoid rings respectively for 200, 400 and 600 rpm. The band 1404 cm\(^{-1}\), 1394 cm\(^{-1}\), 1395 cm\(^{-1}\) is attributed to the ring stretching combined with C-N stretching for 200, 400 and 600 rpm. Bands at 1255 cm\(^{-1}\), 1077 cm\(^{-1}\), 1260 cm\(^{-1}\) and 1073 cm\(^{-1}\), 1261 cm\(^{-1}\), 1081 cm\(^{-1}\) are due
to C= N stretching and in plane bending of the C–H bond, respectively for 200,400 and 600 rpm[6-8]. The C-H out of plane, bending vibration appear at 958, 960, 961 cm⁻¹ respectively for 200,400 and 600 rpm [9].

The different peaks obtained for N-H stretching vibration, nitrogen bond between benzoid and quinoid rings, C-N, C–H, C= N stretching, C-H out of plane in the backbone of polymer PANI shows very slightly shift of the corresponding values of different stretching bands, it may be due to changing mechanical stirring rate of reaction solution [10].

5.5 Conductivity measurement of PANI film by using four-probe method:

The primary means of characterizing prepared PANI film was carried through d.c. conductivity measurements. The measurement of d.c. conductivities was accomplished through use of the 4-probe van der Pauw technique. Under this method, four conductive metal probes are placed in line on the surface of the film; current is injected and collected through the two outer probes, while the potential drop between the two inner probes is monitored simultaneously [11]. During the actual measurement, the resistivity of conducting PANI film was determined from four-probe technique by using standard formula as follows. In the four-point measurements, a four-point probe with the distances between electrodes(S=0.2 cm) was pressed to a thin film on a silicon substrate. The current-voltage characteristics were measured with a digital multimeter [12-13].

5.5.1 Conductivity of PANI film prepared by oxidative polymerization:

The corrected resistivity \( \rho_o \) of the PANI film is,

\[
\rho_o = \frac{V}{I} \cdot 2 \pi S
\]

\[
= 16.50 \times 2 \times \pi \times 0.2
\]

\[
= 20.7372 \text{ Ohm.cm}
\]

But, the resistivity \( \rho \) of the PANI film (at ambient temperature) is expressed as,

\[
\rho = \frac{\rho_o}{G7} (\text{W/S})
\]

\[
= \frac{20.7372}{28.2917} = 0.73302 \text{ Ohm.cm}
\]
Based on the above calculated value of resistivity ($\rho$), the conductivity ($\sigma$) of PANI film was obtained using following formula,

$$\textbf{Conductivity} \ (\sigma) = \frac{1}{\rho}$$

$$= \frac{1}{0.73302}$$

$$= 1.36 \ \text{S/cm},$$

Where the following symbols have their usual meaning as,

$\rho_o =$ Corrected resistivity, \ $\rho =$ Resistivity (Ohm.cm)

$\sigma =$ Conductivity (S/cm), \ $S =$ Probe Distance (cm)

$W =$ Film Thickness (cm), \ $T =$ Temperature (Kelvin)

$G7 =$ Correction Divisor, \ $V =$ Voltage

$I =$ Current

**5.5.2 Conductivity of PANI film prepared by emulsion polymerization:**

The corrected resistivity ($\rho_o$) of the PANI film is,

$$\rho_o = \frac{V}{I} \cdot 2 \pi S$$

$$= 14.47 \times 2 \times \pi \times 0.2$$

$$= 18.1858 \ \text{Ohm.cm}$$

But, the resistivity ($\rho$) of the PANI film (at ambient temperature) is expressed as,

$$\rho = \frac{\rho_o}{G7} \ (W/S)$$

$$= \frac{18.1858}{28.2917}$$

$$= 0.6427 \ \text{Ohm.cm}$$

Based on the above calculated value of resistivity ($\rho$), the conductivity ($\sigma$) of PANI film was obtained using following formula,

$$\textbf{Conductivity} \ (\sigma) = \frac{1}{\rho}$$

$$= \frac{1}{0.6427}$$

$$= 1.55 \ \text{S/cm}$$
The following, Table 5.1 indicate the resistivity and corresponding conductivity values of prepared PANI films by both polymerization processes.

**Table 5.1: Resistivity and corresponding conductivity of PANI films**

<table>
<thead>
<tr>
<th>Method of polymerization</th>
<th>Corrected resistivity of PANI film (ohm.cm)</th>
<th>Resistivity of PANI film (ohm.cm)</th>
<th>Conductivity of PANI film (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidative</td>
<td>20.7372</td>
<td>0.73302</td>
<td>1.36</td>
</tr>
<tr>
<td>Emulsion</td>
<td>18.1858</td>
<td>0.6427</td>
<td>1.55</td>
</tr>
</tbody>
</table>

The measured conductivity values of PANI films were observed to be 1.36 S/cm and 1.55 S/cm. These values show good agreement with the values reported by Jonas Tokarsky et al. Further this confirmed that the synthesized PANI by both polymerization processes having conducting nature [14].

**5.6 Ellipsometry characterization:**

The ellipsometry is particularly used for the analysis of thin films, bulk materials and surfaces [15]. The main advantages of this technique is that it is a non-destructive optical method and small changes in thickness (< 2 nm) and refractive index (< 0.005) can be easily detected by using this technique [16]. In recent technology, the thickness of thin and ultra thin films is found to be important design parameter. Hence there exists a great need for characterizing and understanding the thickness dependence properties of thin films [17]. The refractive index (R.I.) and thickness of deposited PANI films prepared from oxidative and emulsion polymerization were observed through ellipsometer (SD-Philips 1010) system having a source of He-Ne LASER with wavelength 632.8 nm in our laboratory.

The R.I. and thickness topography of deposited PANI films determined from ellipsometry are shown in following Fig. 5.3 and 5.4. The Fig. 5.3 (a) indicates R.I. while Fig. 5.3 (b) indicates thickness of the PANI film for oxidative polymerization and Fig. 5.4 (a) indicates R.I. while 5.4 (b) indicates thickness of the PANI film for emulsion polymerization respectively. It was noted that Figures 5.3 (b) and 5.4 (b) shows the uniform thickness of the deposited films. The results obtained with this model system are
quite encouraging. The results demonstrate the potential of the ellipsometric technique for characterization of bulk interactions of organic molecules that are covalently linked to the polymer backbone [16].

Figure 5.3 (a): R. I. topography of the PANI (Oxidative polymerization) film

Figure 5.3 (b): Thickness topography of the PANI (Oxidative polymerization) film

The average R.I. and thickness of the PANI films is determined to be 1.54 and 470.99 Å respectively for the films prepared by oxidative polymerization while the average R.I. and thickness of the PANI films is determined to be 1.88 and 480 Å respectively for the films prepared by emulsion polymerization. It was found that the R.I. increases from 1.54 to 1.88 with increasing film thickness from 470.99 to 480 Å. It happens due to lower densities and lack of continuity or homogeneity of the film. The dependence of R.I.
caused by the interference phenomenon is due to the film’s morphology and molecular chain orientation. The changes in the value of R.I. may also be attributed to factors such as the crystallinity, electronic structure, density and defects [17].

Figure 5.4 (a): R. I. topography of the PANI (emulsion polymerization) film

Figure 5.4(b): Thickness topography of the PANI (emulsion polymerization) film

5.7 Current–Voltage (I-V) characteristics of PANI films:

I-V characteristic of PANI film was studied by measuring the current with varying voltage at room temperature. This study is essential to ensure whether the PANI film possesses the ohmic contact or rectifying contacts [18]. Fig. 5.5 shows a combination of I-V characteristic curves consisting one curve of oxidative and three curves of emulsion polymerization (i.e. at 200, 400 and 600 rpm) of PANI films.
Figure 5.5: I-V characteristic curves of PANI film

In the present I–V characterization an ohmic current was observed with a symmetric current in both positive and negative voltage ranges [3]. All the four measured I-V characteristics are linear and ohmic contacts between the polymer and the electrodes are formed. The linear relationship of the graph revels that the PANI film has an ohmic behavior [19]. Further it was observed that, all films are stable to environmental with stability up to 3-4 months at room temperature [20].

5.8 SEM analysis of HCl doped PANI film:

Figure 5.6 SEM image of HCl doped PANI film

The surface morphology of the HCl doped PANI film was studied by Scanning Electron Micrograph (SEM). The figure 5.6 shows the SEM image of HCl doped PANI
(oxidative) film taken at and 1 μm scale. The synthesized film exhibits uniform, porous, and granular surface morphology. Another film of PANI was found to be single phase, homogeneous and uniform compact globular structure. It was observed for PANI composition synthesized by oxidative polymerization, of three different magnifications taken at 10, 5 and 1 μm scale as shown in Fig.5.7, Fig.5.8, Fig. 5.9 respectively [3].

Figure 5.7 SEM image of PANI film (10 μm scale)

Figure 5.8 SEM image of PANI film (5 μm scale)
One can see from the SEM micrographs that the samples are predominantly granular and the grain sizes are in the range of 1-2 μm. From all the SEM images of the samples, it is seen that a significant amount of clustering exist between these grains. In presence of such clustering, SEM cannot resolve the individual grains [21]. The high porosity and granular surface morphology is important for gas sensing applications. In view of these characteristics SEM results suggest the applicability of PANI matrix for gas sensor [22].

**5.9 Transmission Electron Microscopy (TEM) of PANI synthesized using Oxidative polymerization:**

Fig. 5.10 (a) and (b) shows the Transmission Electron Microscopy (TEM) of PANI synthesized using oxidative polymerization method for two samples. The TEM image shows lamellar (d=200-300 nm) [23].
Figure 5.10 (a): TEM images of PANI (Oxidative polymerization)

![TEM images of PANI (Oxidative polymerization)](image)

Figure 5.10 (b): TEM images of PANI (Oxidative polymerization)

Table 5.2: Size of nanoparticles and corresponding number of PANI particles

<table>
<thead>
<tr>
<th>Diameter in (nm)</th>
<th>Total number of PANI particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>50-100 (A)</td>
<td>2</td>
</tr>
<tr>
<td>100-150 (B)</td>
<td>2</td>
</tr>
<tr>
<td>150-200 (C)</td>
<td>8</td>
</tr>
<tr>
<td>200-250 (D)</td>
<td>8</td>
</tr>
<tr>
<td>250-300 (E)</td>
<td>2</td>
</tr>
<tr>
<td>300-350 (F)</td>
<td>9</td>
</tr>
<tr>
<td>350-400 (G)</td>
<td>3</td>
</tr>
<tr>
<td>400-450 (H)</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 5.10 (c): Graphical representation of particle diameter Vs No. of PANI particles
5.10 Transmission Electron Microscopy (TEM) of PANI synthesized using emulsion polymerization:

The TEM images of the PANI nanoparticles are shown in Fig. 5.11, 5.13 and 5.15 for different stirring rate 200 rpm, 400 rpm, 600 rpm respectively. Figure shown in figure 5.12, 5.14 and 5.16 shows the particle size distribution histogram for different stirring rate 200 rpm, 400 rpm, 600 rpm respectively. The size distributions were very narrow as shown in histogram. The TEM image shows a dispersed nanoparticle (d=10-20 nm), adherent nanoparticle (d=30-40 nm), lamellar (d=200-300 nm) and dendritic (diameter of 40 nm) [23]. TEM of PANI film exhibited a nanospherical-like morphology with particle diameter around 50 nm [1]. The figure shows maximum frequency of particle sizes, around 20-30 nm, for 200 rpm. For 400 rpm and 600 rpm the average particle size was found to be same i.e. 80-100 nm, however for 600 rpm the granules are more in number. The average particle size increases from 20-30 nm to 80-100 nm (as shown in table 5.3, 5.4 and 5.5). Further as we proceed from 200 rpm to 600 rpm, the spherical granules show some trend to align along a particular direction. Mostly the polyaniline nanoparticles formed are larger in size, possibly because large number of particles aggregated (Xia and Wang 2002) to form larger sized particles [24].

![Fig. 5.11 TEM image of PANI nanoparticle at 200 rpm](image-url)
Table 5.3: TEM analysis of PANI at 200 rpm

<table>
<thead>
<tr>
<th>Diameter in (nm)</th>
<th>Total Number of PANI particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-30 (A)</td>
<td>10</td>
</tr>
<tr>
<td>30-40 (B)</td>
<td>3</td>
</tr>
</tbody>
</table>

Fig 5.12 TEM histogram of PANI nanoparticle for 200 rpm

Figure 5.13 TEM image of PANI nanoparticle at 400 rpm

Table 5.4: TEM analysis of PANI at 400 rpm

<table>
<thead>
<tr>
<th>Diameter in (nm)</th>
<th>Total Number of PANI particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>60-80 (A)</td>
<td>2</td>
</tr>
<tr>
<td>80-100 (B)</td>
<td>5</td>
</tr>
</tbody>
</table>
Figure 5.14 TEM histogram of PANI nanoparticle for 400 rpm

![TEM histogram of PANI nanoparticle for 400 rpm](image1)

Figure 5.15 TEM image of PANI nanoparticle at 600 rpm

![TEM image of PANI nanoparticle at 600 rpm](image2)

Table 5.5 TEM analysis of PANI at 600 rpm

<table>
<thead>
<tr>
<th>Diameter in (nm)</th>
<th>Total Number of PANI particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>60-80 (A)</td>
<td>2</td>
</tr>
<tr>
<td>80-100 (B)</td>
<td>5</td>
</tr>
<tr>
<td>100-120 (C)</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 5.16 TEM histogram of PANI nanoparticle for 600 rpm

Figure 5.17 shows corresponding selected area electron diffraction (SAED) pattern of PANI. The blurred bright electron diffraction rings show that the polyaniline film is amorphous or poorly crystalline. The SEAD pattern reveal the diffraction ring from core to shell which are indexed as (1 1 1), (2 0 0) confirming fcc structure of PANI [25].

5.11 X-Ray Diffraction of PANI synthesized by Emulsion polymerization:

X-ray diffraction (XRD) technique was employed to characterize the structures of the chemically synthesized PANI films. The XRD patterns were recorded in 2θ range of the order of 10-80°. Following figures indicate the pattern of PANI film includes three prominent broad peaks and few smaller peaks riding over a broad hump, indicating that
chain ordering is predominantly limited to short range [11, 26]. Li et al reported that
crystallinity and orientation of conducting polymers have been of much interest because
highly ordered systems can display metal-like conductive states. Figure 5.18, 5.19 and
5.20 shows the XRD pattern of PANI synthesized at different stirring i.e. 200, 400 and
600 rpm respectively. The XRD of emeraldine form of PANI prepared by using methanol
has peaks at $\theta = 15, 20$, and $24^\circ$. All the three peaks are observed at 19.02, 21.35 and
25.27 values of $\theta$ along with other prominent peaks. The shifting in position is due to
different crystalline behavior and structure on PANI. The result reveals the strong
crystalline nature of synthesized PANI [27].

For PANI the characteristics peaks appeared at 21.35 and 25.27 corresponds to
(020) and (200) crystal planes of PANI [28]. The peak at 25.27 may be ascribed to
periodicity parallel to the polymer chain (Moon et al. 1989). This peak may also represent
the characteristic distance between the ring planes of benzene rings in adjacent chains or
the close contact interchain distance (Pouget et al. 1995). The characteristic broadening
of the observed peaks implies the nanocrystalline nature [25].

The broad peaks observed at about $\theta = 19^\circ$ and $25^\circ$ are similar to those observed
by other researchers [29]. The diffraction pattern of PANI thin film shows a peak at about
$\theta = 19^\circ$ [30] and a hump around at $\theta = 25^\circ$ which is typical for conducting amorphous
polymer [31].

Table 5.6 gives the $2\theta$ scale and peak intensity at different solution stirring rate.
From table it is observed that as increase in stirring rate the peak intensity also increases.
The increase in peak intensity reveals the refinement in crystal structure of the PANI.

<table>
<thead>
<tr>
<th>Solution stirring rate (rpm)</th>
<th>2θ angle</th>
<th>Peak intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>19.1</td>
<td>670</td>
</tr>
<tr>
<td></td>
<td>20.6</td>
<td>780</td>
</tr>
<tr>
<td></td>
<td>25.3</td>
<td>610</td>
</tr>
<tr>
<td>400</td>
<td>19.03</td>
<td>1050</td>
</tr>
<tr>
<td></td>
<td>21.31</td>
<td>1120</td>
</tr>
<tr>
<td></td>
<td>25.27</td>
<td>950</td>
</tr>
<tr>
<td>600</td>
<td>19.5</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>21.0</td>
<td>1250</td>
</tr>
<tr>
<td></td>
<td>25.7</td>
<td>1000</td>
</tr>
</tbody>
</table>
Figure 5.18: XRD spectra for 200 rpm level of PANI synthesis

Figure 5.19: XRD spectra for 400 rpm level of PANI synthesis

Figure 5.20: XRD spectra for 600 rpm level of PANI synthesis
5.12 NMR Spectroscopy:

NMR spectroscopy is a very efficient technique to study the changes in electron density around a given nucleus [21]. The H-Nuclear Magnetic Resonance (NMR) measurement presented here was carried out on a 300MHz NMR spectrometer for PANI in DMSO at Diya Labs, Mumbai. Additional information about the monomer and synthesized polymer structures were obtained from NMR spectra. The Fig 5.21 and 5.22 shows the NMR spectra of PANI synthesized by emulsion polymerization. The extremely intense peaks appearing at 2.5 and 3.5 ppm correspond to the unlabelled DMSO and water present in the solvent, respectively. Apart from these signals, we also observed the peak at 7.075 ppm is due to the protons on the benzene ring [32]. Whereas non-reduced form of the product (Emeraldine base) gave an H-NMR spectra with slight shift of the peak positions (i.e. NH protons appear at 3.65 ppm). The down field signals centered at 7.2 ppm are due to four aromatic protons of the pure reduced form (leucoemeraldine base) [33]. The aromatic protons of the phenylene moiety appear at 6.90 ppm. The protons of the other methylene groups appear at 1.23-3.657 ppm, and the terminal methyl group appears at 0.84 ppm. The peaks associated to the protons on the aniline units are difficult to be assigned. This is because of the delocalized electron or charged species [34].

![NMR spectra of PANI.](image)

**Figure 5.21:** NMR spectra of PANI.
The corresponding structures are shown in Fig. 5.23 [35]. The experimentally observed chemical shifts are in perfect agreement with structure as shown in figure. The poor solubility of PANI in other solvents did not allow us to confirm this fact [32].

5.13 Ammonia Gas Sensing Behavior of PANI:

5.13.1 Mechanism of interaction between PANI and ammonia:

PANI is a polymer, which shows a reversible acid/base doping process. In the acid doped or emeraldine salt (ES) state of PANI is conductive, while in the emeraldine base (EB) or dedoped state of PANI is insulating. The emeraldine salt on treatment with base (ammonia vapors) can be converted to emeraldine base, which on reaction with acid...
(HCl vapors) gets reconverted to emeraldine salt. Thus it shows that these two states are interconvertable [36].

When PANI interacts with NH₃, the following reversible reaction occurs.

\[
\text{PANI}^+ + \text{NH}_3 \leftrightarrow \text{PANI} + \text{NH}_4^+
\]

In the presence of ammonia this reaction goes predominantly towards the right, as NH₃ molecules releases protons from the PANI, thus forming energetically more favorable NH₄⁺. It is the PANI de-doping (de-protonation) reaction. But in the air (with no ammonia) the above reaction begins towards left. Figure shows 5.24 the mechanism of interaction between PANI and ammonia.

\[\text{Figure 5.24: Mechanism of interaction between PANI and ammonia.}\]

Ammonium de-composes into ammonia and protons which being added to PANI molecules, restore the initial level of doping. In this way reversibility of the ammonia on PANI occurs. In fact, in this case we are dealing with chemical bonding [37]. This confirms the fact that the process of ammonium ion (NH₄⁺) formation is accompanied by an energy gain because it has a more stable tetrahedral configuration. On the other hand, the reverse process (gaining protons by PANI) is also energetically favorable. Its nitrogen atoms have sp² hybridized electron orbital, so formation of a third bond with a hydrogen atom is accompanied by a lowering of the total energy of the polymer chain. Thus when
ammonia interacts with PANI, two competing processes of proton gain (by ammonia and by PANI) occurs. Since the heat of ammonia adsorption onto PANI is low, the probabilities of the two processes are more or less the same. The result is that ammonia gets adsorbed onto PANI backbone. This reaction leads to the deprotonation of PANI nitrogen atoms, supporting the disappearance of charge carriers which causes increase in electrical resistance.

5.14 Sensitivity measurement for NH₃ gas:

The ammonia gas sensing characteristics of PANI films was studied under static gas chamber by indigenously developed system at Intelligent Materials Research Laboratory (prior known by Nanoscale Electronics Research Laboratory), Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad – 431 004 (MS) India. Performance of the sensor was determined by measuring its response to various concentrations of liquid ammonia introduced in the chamber. The sensing element was kept on Four-Probe assembly in the gas chamber. The known volume and concentration of ammonia gas was introduced in the chamber which allows PANI film to interact with ammonia gas of desire concentration in ppm. The corresponding change in surface resistance of PANI film was recorded as a function of time. The change of resistance of PANI film when it is exposed to ammonia gas was demonstrated in terms of \( \frac{\Delta R}{R_0} (\%) \); where \( R_0 \) is the initial resistance of the PANI film and \( R \) is the change of resistance of the same film when it is exposed to ammonia gas. The concentration of ammonia gas was varied from minimum value 50 ppm to maximum 1000 ppm. We observed increase in the resistance of PANI film when it was exposed to ammonia gas. The nitrogen atom of the ammonia molecule is responsible for coordinating with the dopants proton enabling its sensing characteristics. The nitrogen-free doublet of ammonia molecules can create a coordinate bonding with the free atomic orbital of the dopants proton [38].

Thus when ammonia interacts with PANI, two competing processes of proton gain (by ammonia and by PANI) occurs. The probabilities of the two processes are more or less the same because the heat of ammonia adsorption onto PANI is low. The results revealed that ammonia gets adsorbed onto PANI film. It shows maximum responses at higher concentrations of ammonia because the number of molecules striking over the
polymer increases as the concentration increases from 50 ppm to 1000 ppm [39]. The results obtained so far are explained in detail as below.

The ammonia gas sensing tendency of a PANI film was studied by using the gas sensor set up. The prepared PANI film was placed inside the measuring chamber and closed airtight. Air was passed through the chamber followed by passing ammonia gas mixed with air in specific proportions. The constant current was passed through the PANI film by a constant current source and the corresponding voltage was measured at an interval of 30 sec. Then ammonia gas flow was stopped. After cut off of the ammonia gas flow, the resistivity falls and then remains constant. Again the gas was passed and the complete process was repeated. Electrical resistivity measurements were recorded for PANI-film when the film was exposed to NH₃ gas. The sensitivity of the sensor may be defined as the ratio of the change of resistivity due to exposure to the gas under testing to the resistivity of the sample in the air. The percentage sensitivity is calculated by equation (1) [18].

\[
S(\%) = \frac{R_o - R_g}{R_o} \times 100 \quad \ldots \ldots (1)
\]

Where, \( R_g \) is the resistance monitored in presence of NH₃ gas (resistance after exposure to ammonia) and \( R_o \) is the resistance monitored in the air (resistance before exposure to ammonia). Planer electrical resistivity of PANI film was monitored across the two parallel strip silver pasted electrodes separated by 2 mm spacing. The obtained results shown in Table 5.7 have good agreement with the results reported by Duong Ngoc Huyen and group [40].

Table 5.7: Response of PANI film to ammonia

<table>
<thead>
<tr>
<th>Conc. of NH₃ in ppm</th>
<th>Resistance of PANI film(MΩ) before exposure of NH₃<a href="Pristine">R₀</a></th>
<th>Resistance of PANI film(MΩ) after exposure of NH₃[R₉]</th>
<th>Sensitivity of PANI film in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>5.240</td>
<td>5.298</td>
<td>1.106</td>
</tr>
<tr>
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Further the deposited conductive PANI thin films have been used for detection of ammonia gas. The prepared film shows good response on exposure to ammonia environment. It indicates the variation in the resistance between the electrodes of the PANI film, which was measured as a function of ammonia gas concentration after the exposure in the chamber at ambient pressure and temperature. The obtained values of resistance in air and in ammonia environment are presented in table 5.7. The plot of concentration of ammonia gas in (ppm) against percentage sensitivity is shown in figure 5.25. It shows that, the magnitude of percentage sensitivity linearly increases with the concentration of ammonia from 200 to 1000 ppm. The highest percentage sensitivity around 39.13% of the PANI film was observed at higher concentration 1000 ppm of NH₃ gas. Polyaniline by chemical method was used as ammonia gas sensor by the other research groups [41].

Lot of studies is dealing with the improvement of sensitivity and selectivity of PANI sensors. The parameters showing an influence on these two factors are the nature of the dopant, the presence and the nature of substituants on aniline ring, the deposition method of sensitive layer, the PANI post-treatment by an organic vapor, and the use of a composite sensitive film with PANI. Other parameters like electrode geometry [42] and temperature [43] influence the response of gas-sensitive chemo-resistors. Moreover, the polymer swelling can participate to the gas response [44]. Kukla et al showed a decrease
of the polymeric sensor sensitivity when the temperature increased from 27 to 78°C, thereby proving that desorption is favored compared to adsorption. Another drawback is the limited lifetime of the sensor exposed, for example, to ammonia (NH₃) vapors [37].

5.14.1 Responses of PANI films at different concentration of ammonia:

The sample in the form of PANI thin film was placed in ammonia gas chamber, and the sensor response was monitored. All PANI films were tested for ammonia gas at room temperature. The polymer PANI used here for the preparation of film was synthesized by oxidative polymerization. The responses of the 5 different PANI films (with same dimension parameters) to various concentrations of ammonia are shown in Fig. 5.26 (a) (b) (c) (d) and (e). The exposure to NH₃ was repeated, for 100ppm, 200ppm, 300ppm, 400ppm, 500ppm and the individual responses were studied. For every time the gas was replaced by ambient air, so as to evacuate the chamber. It was observed that, the resistance of the samples first increased sharply, and then gradually decreased when the ammonia gas was replaced by air.

![Graph](image)

Fig. 5.26 (a): The response of the sample during ammonia admission removal cycle at 100 ppm ammonia concentration.
Fig. 5.26 (b): The response of the sample during ammonia admission removal cycle at 200 ppm ammonia concentration

Fig. 5.26 (c): The response of the sample during ammonia admission removal cycle at 300 ppm ammonia concentration
Fig. 5.26 (d): The response of the sample during ammonia admission±removal cycle at ammonia concentration: 400 ppm

Fig. 5.26 (e): The response of the sample during ammonia admission removal cycle at ammonia concentration: 500 ppm

These curves are characterized by high reproducibility and short relaxation times. The time for the resistance build-up is nearly 1 min, while the resistance drop (when regeneration in the air occurs) proceeds more slowly. As shown in Fig 5.26, the one-cycle curves (sensor response to ammonia intake followed by its regeneration in air) of the sample demonstrate that the steady-state value of the sample's resistance. It shows maximum responses at higher concentrations of ammonia because the number of molecules striking over the polymer film increases as the concentration increases from 100 ppm to 500ppm respectively. The calibration plots for different ammonia
5.15 Gas sensing characteristics:

5.15.1 Ammonia gas sensing behavior of PANI film prepared by Oxidative polymerization:

The sample in the form of PANI thin film was placed in ammonia gas chamber, and the sensor response was monitored. The polymer PANI used here for the preparation of film was synthesized by oxidative polymerization. The results were observed in terms of the change in resistivity of the polymer film. Fig. 5.27 shows the sensing behavior of PANI films. In order to get the recovery time of the polyaniline gas-sensor, the gas flow was stopped after it reached the saturation level, followed by 5 min purging with air. A fixed amount (corresponding to proportions of 100 ppm) of NH₃ gas was injected into the test chamber, and film resistance measured with respect to time, until it reached a steady value. The increase of concentration enhances the rate of diffusion of ammonia molecules towards and into the polymer PANI thin film. It shows maximum responses at higher concentrations of ammonia because the number of molecules striking over the polymer increases as the concentration increases from 100 ppm to 500 ppm.

![Figure 5.27: Ammonia sensing behavior of PANI film.](image-url)
5.15.2 Response Time and Recovery Time:

Figure 5.28 shows the recovery and response time of PANI film at different ammonia concentration. From figure it reveals that the recovery and response time seems to increase with the increase of ammonia concentration. The increase of NH₃ concentration increases the quantity of adsorbed ammonia molecules on the PANI surface to obtain the equilibrium of NH₃ concentrations, then increasing probably the time for the complete desorption of the ammonia molecules from the PANI layer [45]. At 100ppm concentration of ammonia, the recovery time found to be around 1000sec, while it observed to be increased linearly up to 7000sec for 500ppm concentration. On the other hand the response time found to be increased from 850sec to 2000sec.

![Figure 5.28: Recovery and response time of PANI film at different ammonia concentration](image)

5.15.3 Sensitivity of PANI film:

The sensitivity of PANI sensitive layer at different ammonia concentration is represented in Fig. 5.29. The sensitivity of this sensor observed to be increases with increasing NH₃ concentration. The sensitivity at 100ppm of NH₃ was measured about 2.5% and it linearly increases up to 24% at 500ppm concentration. Indeed, the structure of PANI has a significant number of reactive sites (polarons) for the detection of the NH₃ molecules [46].
5.16 Ammonia gas sensing behavior PANI film prepared by Emulsion polymerization:

Fig. 5.30 shows the sensing behavior of PANI films. The polymer PANI used here for the preparation of film was synthesized by emulsion polymerization.

From figure it is observed that as increase in time of exposure the sensitivity observed to be increases. At 50ppm the sensitivity found to be 3.5% and increased linearly up to 28.5% for 500ppm concentration.
5.16.1 Response Time and Recovery Time:

Fig. 5.31 shows the recovery and response time of PANI film at different ammonia concentration.

![Graph showing recovery and response time of PANI film](image)

**Figure 5.31: Recovery and response time of PANI film at different ammonia concentration**

From figure it reveals that the recovery time seems to be increased as increase in NH$_3$ concentration up to 200ppm and further it become steady onwards from 200ppm up to 500ppm. The response time of PANI film seems to increase with the decreases of ammonia concentration. The response time observed to be decreases from 800sec to 200sec for increase in NH$_3$ concentration from 50 to 500ppm respectively. The number of molecules that diffuse with the sensing sites on the film in a given time increases, and therefore the response time decreases. Increasing concentrations lead to increased chemisorbed ammonia, which in turn enhances the desorption rates and sensing site renewal [18].
5.16.2 Sensitivity of PANI film:

The sensitivity of PANI sensitive layer at different ammonia concentration is represented in Fig. 5.32.

![Sensitivity Graph](image)

**Figure 5.32: Sensor sensitivity as a function of ammonia concentration**

The sensitivity of this sensor observed to be increases with increasing NH$_3$ concentration. The sensitivity at 100ppm of NH$_3$ was measured about 3.5% and it linearly increases up to 29% at 500ppm concentration.

**Equation:** \( y = a + b\times x \)

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