Chapter 4
Deposition of Conducting Polymer Thin Films

4.1 Introduction:

Conducting polymers, such as polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy), and their derivatives, have been used as the sensitive layers of gas sensors since early 1980s [1]. Conducting polymers have gained popularity as important sensing materials for various organic vapors, hazardous gases, and humidity. They used as a material for fabricating sensor devices because of their applicability at room temperature. In comparison with most of the commercially available sensors, which are based usually on metal oxides and operated at high temperatures, the sensors made of conducting polymers have many improved characteristics. They have high sensitivities and short response time; particularly these features are ensured at ambient temperature [2]. The high conductivity is recognized to the more regular structure of the doped polymers like PANI. An additional advantage of PANI is that it can be made processable. Doped PANI can be made soluble in common organic solvents by a proper choice of the dopant-solvent combination, thus enabling the formation of transparent conducting films by simple methods such as spin coating and dip coating [3]. With respect to potential applications, the deposition of a conducting polymer as thin film (on a substrate or free standing) or as a thick coating is advantageous. Unfortunately, PANI in the conducting state is hardly dissolved in any solvent or melted below the decomposition temperature. In order to increase the solubility of PANI, the protonation of PANI with organic acids having a bulky hydrocarbon as dodecyl benzenesulfonic acid, or the addition of various surfactants as reaction components, has been tried [4-6]. For achieving maximum gas sensitivity, CP compounds are usually studied as thin films. Among the doped conductive polymers that have been widely investigated are PPy and PTh but unfortunately these materials are not readily processible. In contrast, PANI is soluble in organic solvents from which free-standing films can be easily cast [7].

In present research work, PANI was processed into thin-film form using spinning technique. The gas sensitivities of the different films are compared. The technique spin coating is a simple process for rapidly depositing thin coatings onto flat substrates. The
substrate to be covered is held by some rotatable fixture (using vacuum to clamp the substrate in place), and the coating solution is dispensed onto the surface, the action of spinning causes the solution to spread out and leave behind a very uniform coating of selected material on the surface of the substrate. In brief, an excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. A machine used for spin coating is called a spin coater. [8]. Spin coating has been used for several decades for the application of thin films. This method was first described by Emslie et al. (1958) and Meyerhofer et al. (1978). The spin coating technique was preferred for the present work, though this technique has various advantages (discussed in 2.2.3 of Chapter -2).

Conducting polymers are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified suitably by copolymerization or structural derivatives. Furthermore, conducting polymers have good mechanical properties, it allow a superficial fabrication of sensors. As a result, more and more attentions have been paid to the sensors fabricated from conducting polymers, and a lot of associated articles were published. There are several review articles emphasize on different aspects of gas sensors, and some others discussed sensing performance of certain conducting polymers, but few of them paid special attention to summarizing gas sensors based on different conducting polymers [1]. A variety of conducting polymers have shown notable changes in resistivity on exposure to different analytes. Among the members of this family, PANI is found promising for its ease of preparation, high environmental stability, stable electrical conduction mechanism, and other special properties [9]. PANI is also unique among conducting polymers though it has simple acid / base doping / de-doping Chemistry. It has variety of potential applications including batteries, sensors, anticorrosion coatings, separation membranes etc. In order to detect a chemical vapor, the vapor-PANI interaction must produce a noticeable change in the electrical conductivity of the film. [10]. In the present work, PANI synthesis is based on mixing aqueous solutions of aniline hydrochloride and ammonium persulphate / peroxidisulphate at ambient conditions, followed by the separation of PANI hydrochloride precipitate by filtration and drying. The HCl doped PANI-HCl was also prepared by using emeraldine base PANI with 0.1M ammonium
solution and m-cresol solution at room temperature. [11]. Wan et. al. reported that microtubules of PANI was successfully synthesized by in-situ doping polymerization in the presence of β-naphthalene sulfonic acid as a dopant.[12]

4.2 Chemical Used:

Table 4.1: List of chemical used for experimental work

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Chemical formula</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric Acid</td>
<td>HCl</td>
<td>s d fine chem. ltd.</td>
</tr>
<tr>
<td>Ammonium Persulphate/ peroxidisulphate (APS)</td>
<td>(NH₄)₂S₂O₈</td>
<td>s d fine chem. ltd.</td>
</tr>
<tr>
<td>Aniline Hydrochloride</td>
<td>C₆H₅NH₂.HCL</td>
<td>s d fine chem. ltd.</td>
</tr>
<tr>
<td>NMP (n-methylpyrrolidone)</td>
<td>C₃H₉NO</td>
<td>s d fine chem. ltd.</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>NH₄OH</td>
<td>s d fine chem. ltd.</td>
</tr>
<tr>
<td>Acetone</td>
<td>C₃H₆O</td>
<td>Loba Chem.</td>
</tr>
<tr>
<td>Trichloroethylene (TCE)</td>
<td>C₂HCl₃</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Sodium dodecysulfate (SDS)</td>
<td>CH₃(CH₂)₁₁OSO₃Na</td>
<td>Merck</td>
</tr>
</tbody>
</table>

4.3 Why silicon (Si) substrate:

The use of Si as substrate or transducer allows a mass production of sensors because of the prominent silicon technology. Furthermore, the deposition of thin PANI layers onto silicon can be conducted with various methods; therefore, the choice of the best deposition process for a given application is possible. However, the adherence of organic layers on inorganic substrates is weak and has to be improved. A method to increase PANI adherence on silicon is reported by Daminique Nicolas-Debarnot et al [13]. The Si has ability to get in n-type and p-type form by doping and it easily alters the electronic properties. The electronic, mechanical, thermal and optical properties of Si make it widely applicable for a variety of high-tech industries, including fabrication of sensor device, MEMS, optoelectronic components, and solar cells etc. The availability of Si is moderate and most widely distributed in dusts, sands, planetoids, and planets as different forms of silicon dioxide (silica) or silicates.
Further, the ability to produce highly pure (99.9999999% purity) nearly defect-free single crystalline silicon with high degree of flatness. This makes it a perfect candidate particularly in semiconductor industry [14].

4.4 Experimental process flow:

![Experimental flow chart]

4.4.1 Cleaning of silicon wafer:

It is now well known that the device performance, reliability, and product yield of Si circuits are critically affected by chemical contaminants and particulate impurities on the wafer or device surface. Hence, before the fabrication it is essential to clean the substrate in order to remove the contamination and improve surface conditioning to achieve a good quality of films. Generally, it is observed that all the wafer cleaning processes are done in liquid phase due to several advantages including high solubility of chemical reagents and contaminants, metal complexation and easier avoidance of electrostatic deposition of particles compare with air [9]. The cleaning process of Si wafer substrate, which is used for the deposition of films involves following methods.
Wafer cleaning process performed in the present work:
In present work, before the deposition of thin films, the following procedure is utilized for cleaning the surface of Si wafer substrate.

- Sample were etched for 30sec in dilute buffer HF [1:10 HF: H₂O] to remove out the local oxide from the surface of wafer.
- Rinse in de-ionized (DI) water.
- Heat treatment for 5 min. in Trichloroethylene (TCE)
- Rinse in DI water.
- Heat treatment for 5 min. in Acetone.
- Rinse in DI water.
- Heat treatment for 5 min. in Methanol.
- Final rinse in de- ionized DI water

4.5 Experimental Methods: Synthesis of PANI:

4.5.1 Oxidative polymerization of PANI:

The PANI synthesis is based on mixing aqueous solutions of aniline hydrochloride (C₆H₈CIN) and ammonium peroxydisulfate (NH₄)₂S₂O₈ at ambient conditions, followed by the separation of PANI hydrochloride precipitate by filtration and drying. For this synthesis, we have selected hydrochloric acid in equimolar proportion to aniline i.e. aniline hydrochloride has been used as a monomer. The handling of solid aniline salt was preferred to liquid aniline from the point of view of toxicity hazards. Peroxydisulfate is the most commonly used oxidant, and its ammonium salt has been preferred because of its better solubility in water. The concentration of aniline hydrochloride was set to 0.2 M. The stoichiometric peroxydisulfate/aniline ratio of 1:25 is optimized to obtain the best yield of PANI. The oxidative polymerization process is carried out by stirring the solution of Aniline hydrochloride (2.59 gm) and Ammonium peroxydisulfate (5.71 gm) dissolved in 50 ml distilled water separately.
Figure 4.2: Process flow chart for chemical synthesis of PANI

Then both the solutions were mixed to initiate process of polymerization. As the polymerization of aniline is an exothermic reaction, temperature rises with the progress of polymerization. After stirring for 1 hour, the solution was kept to rest over a night. The PANI precipitate formed after overnight aging have been collected and washed thrice with 100ml portions of 0.2M HCl, and similarly with acetone. Washing the PANI precipitate with 0.2M HCl removes oxidant, residual monomer and its decomposition products. A final washing was done with acetone that removes low molecular weight organic intermediates and oligomers. It also prevents the aggregation of PANI precipitate during drying, and the product was obtained in a fine powder form. This synthesized greenish PANI (emeraldine) hydrochloride powder is then dried in air and stored in a container. The resulted emeraldine salt was subsequently treated with NH₄OH (1M) to
make it emeraldine base, which showed better solubility in an appropriate solvent. This precipitate was washed with water and acetone and dried for 6-8 hours [15].

![Chemical reaction equation](image)

**Figure 4.3 (b) Oxidation of aniline hydrochloride with ammonium peroxydisulfate yields PANI [15]**

![Image of beaker with solution](image)

**Figure 4.4: Beaker containing solution of synthesizing materials during stirring**

### 4.5 Deposition of PANI films:

The active layer of PANI as a sensor was fabricated with the help of spin-coater. The solvent NMP (n-methylpyrrolidone) is a chemically stable and powerful polar solvent hence it was used for the preparation of the PANI films. PANI powder
(synthesized in-house) in the emeraldine base form was dissolved in NMP. The resulting solution appeared blue in reflected light. This was spun onto the interdigitated electrode structure shown in Fig.4.6. Spinning process was undertaken in our lab using a model Milman S 2000 spin coating unit, as shown in figure 4.5

**Figure 4.5: Spin coating unit (Milman S2000)**

### 4.6 Preparation of PANI nanoparticles by emulsion polymerization:

Conducting polymers (CPs) are in use as an alternative to metal oxide materials for gas sensing applications. Among the CPs, PANI has become one of the technologically important CPs, because of its relatively easier synthesis, and for having excellent electronic and electro-chromic properties. It has been used in making organic solar cell, as well as gas sensor applications. However, PANI is not as sensitive as metal oxides towards gas species, and its poor solubility in organic solvents limits its applications. In spite of these problems with PANI, efforts are being made to improve its solubility by involving protonation with organic acids or preparing it using emulsion polymerization in presence of surfactants. There have been several reports on improving PANI’s sensitivity and selectivity by making use of new methods, such as its synthesis in nano-structured forms, or by addition of metal catalysts, and by combination with other polymers [16].
4.6.1 Experimental Procedure:

In the present research study, we synthesize PANI in the form of nanoparticles through emulsion polymerization technique. Under this study, initially 0.49 g (0.0021 m) of APS was dissolved in 10 ml of 0.1 M HCl solution and added drop wise into a mixture containing 0.40 g (0.0043 m) of aniline and 9.80 g (0.034 m) of SDS in 100 mL of 0.1 M HCl solution, at 1.0 mL/min rate. The molar ratio of monomer(s) to APS was kept as 2.0 through all the experiment, and the total volume of mixture after the addition of initiator (APS) was 110 mL. Since the Krafft point of SDS is around 16 °C, the polymerization was performed at 16 ± 0.1 °C with the mechanical stirring in two-neck round bottom flask mounted in a thermostat for 12 hrs. The dark green precipitate of polymer nanoparticles (PANI) was filtered and washed for 2 - 3 times with methanol and then dried in a vacuum oven at 60 °C and 5mm of pressure for 72 hrs. This polymerization was performed at different mechanical stirring rates viz 200, 400, 600 rpm [17].

4.7 Fabrication of PANI sensor:

Increased interest in environmental protection has led to a continuous expansion in sensor development. A sensor is a transducer that converts one form of energy into another form suitable for further processing. Although sensors of a great variety of types are well recognized in process industries, agriculture, medicine, and many other areas, the development of sensing material with high sensing capabilities is proceeding at an unprecedented rate. Numerous materials have been utilized as humidity, organic and inorganic vapor sensors. Sensors based on changes in resistance and capacitances are preferred to conventional ones owing to their compact size, which could facilitate miniaturization required for electronic circuitry [9].

The conducting polymers seem very promising for being used as chemical sensors in terms of the two aspects: these polymers can either be directly used as sensitive elements, or as matrices to immobilize specific agents. The potentialities of electroconducting polymers as sensitive elements are based on modulation of their doping level during redox interaction with some gases. This effect results in an immediately controlled response in conductance [18]. Fig.4.6 shows a schematic diagram of the interdigitated electrode structure prepared and further used in this work.
In present research work, our approach was to obtaining PANI sensor which is based on the chemical polymerization of thin films. Upon film formation a conducting path is formed through the film. Silicon chips of 1x1 cm in size served as the sensor base (substrate). The substrates used in this study were already having metalized electrodes. The PANI as a gas sensitive layer was deposited on the substrates having metalized electrode. The sensor was formed by connecting wire terminals to electrode with silver pasted as shown in Fig. 4.7.

**Figure 4.6: Interdigitated electrode structure** [1]

**Figure 4.7: Silicon substrates forming the basis for an ammonia sensor**
4.8 Experimental setup to detect NH$_3$ gas sensing behavior of PANI film:

![Gas sensing setup](image)

**Figure 4.8: Gas sensing setup**

The ammonia gas sensing characteristics of PANI films was studied by static gas chamber assembly. This part work was carried at Intelligent Materials Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Maharashtra on the gas sensing setup as shown in Fig. 4.8. The films of PANI were tested at room temperature. These films having metallic contacts were kept in the test chamber of known volume with electrical leads taken out for electrical measurements. The sensing element was kept on Four-Probe assembly in the gas chamber. The Four-Probe assembly interfaced with current-voltage (I-V) analyzer [Keithley]. Thereafter a fixed amount of NH$_3$ gas (corresponding to proportions of 100 ppm) was injected into the test chamber, and film resistance measured with respect to time, until it reached a steady value. This procedure was followed once again after removing NH$_3$ and exposing the test chamber to clean air. These steps were repeated for all different films and for different NH$_3$ gas concentrations (ranging from 100–500 ppm).

We also studied response and recovery time of the films with respect to ammonia gas exposure. The response time, and the recovery time are defined as the time required for a film resistance to reach 90% of its saturation value from the starting value on gas exposure, and on removal of the gas, respectively.
4.8 Characterization techniques used:

The physico-chemical characteristics of synthesized conducting polymers are determined using various advanced characterization techniques as listed below.

1. The Fourier Transform Infrared Spectroscopy (FTIR-Nicolet 380) as shown in Figure 4.9 was used to determine chain orientation and structure of polymers and to elucidate mechanism of polymerization of PANI films.

2. The uniformity and thickness of films were measured using the Philips SD-1000 Ellipsometer system shown in Fig. 4.10.

3. To understand electrochromic window and non-linear optical material characteristics, UV-Visible spectroscopy as shown in Fig. 4.11 is used.

4. The surface morphology of the PANI films were studied by using Scanning Electron Microscope (SEM) [JEOL JSM-6360A] as shown in Fig. 4.12.

5. Transmission Electron Microscope (TEM) as shown in Fig. 4.13 was used to study the morphology and particle size of the synthesized PANI obtained through oxidative and emulsion polymerization.

6. The Current-Voltage (I-V) characterization of PANI films were studied by I-V measurement system as shown in Fig 4.14.

7. NMR (H-NMR) was used to verify the structure confirmation, chain orientation and molecular motion of PANI.

8. The XRD as shown in Fig. 4.15 was used to study crystal structure and crystallite size of synthesized PANI.
Figure 4.9: FTIR spectrometer (Nicolet 380)

Figure 4.10: Ellipsometer (Philips SD-1000)
Figure 4.11: UV-1601 (02) Make: Shimadzu, Japan UV spectroscopy

Figure 4.12: Scanning Electron Microscope (SEM) JEOL JSM-6360A
Figure 4.13: Transmission Electron Microscope PHILIPS CM 200

Figure 4.14: Current-Voltage (I-V) analyzer [Keithley]
Figure 4.15: X-Ray Diffractometer
References: