Chapter-II

Experimental Techniques

2.1 Introduction:

In the previous chapter the theoretical background necessary for the work carried out is given. The literature survey gives a bird’s eye view of the present scenario of polymer based humidity sensors from which the aims and objectives of the work have been outlined.

The present chapter describes the experiments carried out for fabrication and characterization of humidity sensor. The experimental work includes IDC structure fabrication, monomer distillation, spin coating, plasma treatment, plasma polymerization, structural characterization by FTIR, the response of the material to relative humidity and optical response of the material.

2.2 Sensor Fabrication:

For the sensor fabrication an interdigitated capacitive (IDC) type sensor structure was selected. As shown in Fig-(2.1) it consists of planer metal electrodes in the interdigitated ID form selected for gathering large value of capacitance and small value of resistance component. The thin film of the sensor material acts as a dielectric between the fingers of the ID structure. The fabrication process is described in following subsections.

![Fig.2.1 Inter-digited capacitor (IDC) pattern](image)

2.2.1 Mask Preparation:

Each finger has length of 8mm and the distance between the successive fingers is 0.3mm. There are total twenty fingers which covered an area of about 0.8 cm². The mask pattern was drawn by art work on white paper. The artwork is drawn on the scale which is ten times the original pattern. The final mask was made using photo-reduction technique that reduces the image by 10 times. The mask was made with Kodak high resolution plate (HRP). Mask
preparation depends on the photo resist being used. In this work negative photo resist was used therefore a positive mask was prepared.

2.2.2. Photo Lithography for pattern delineation

Photolithography is a technique of transferring a mask pattern on to the substrate. In this work mask was given to the fabricator. Then using photolithographic techniques, 50 IDCs were fabricated using glass epoxy copper clad substrate.

2.2.3 Cleaning of Glass, epoxy and silicon Substrates:

Prior to PMMA deposition on glass substrates, the glass substrates (borosilicate glass slides) were cleaned in the following manner:

The substrates were boiled in chromic acid (potassium dichromate dissolved in deionized water plus a few drops of sulfuric acid) for a few min and kept soaked in it for an hour. They were then rinsed in DI water and then cleaned in neutral soap (labogen) solution. They were again rinsed in DI water and ultrasonically cleaned in methanol for a few min.

The epoxy substrates were cleaned by putting them in acetone for 10 minutes. Then wash those using DI water. Silicon substrates were cleaned by putting them in hydrofluoric acid (HF) for 10 minutes. Then remove from HF and clean by tissue paper.

2.3. Deposition of the sensing material:

After the ID pattern was transferred onto glass epoxy copper clad, the sensing materials i.e. spin coated PMMA, plasma treated PMMA and plasma polymerized MMA were deposited on the IDCs, glass, and silicon.

2.3.1 PMMA Deposition by spin coating:

Preparation of PMMA solution

Commercially available PMMA granules (Gujpol India Ltd.) were dissolved in AR-grade chloroform and subsequently spin coated onto previously cleaned IDC structures on glass epoxy and glass substrates. In order to vary the viscosity of the liquid 0.1gm, 0.2gm, 0.3gm of PMMA granules were dissolved in 10ml of chloroform.
Spin coating and thickness measurement

For the spin coating of the PMMA, the commercially available PMMA granules (Gujpol India Ltd.) were dissolved in AR-grade chloroform and subsequently spin coated onto previously cleaned IDC structures (where the PMMA got deposited in between the ID fingers) and glass substrates. The thickness of the copper ID is about 34 µm. A Laurell’s (WS-400-6NPP-LITE) spin coating system (fig.2.2) was used in this study. Spin coating was achieved by pouring the solution on a clean substrate to fully cover it. After selecting the spin speed of the coater, it was switched on to start spinning. The spin speed used in the experiments was varied between around 500-3000 rpm. The spin coating duration for all samples was 60 seconds. To remove the extra solvent from the layer, the samples were placed in the oven at a temperature of 60 °C for 20 minutes after spin coating.

Several experiments were carried out. Different concentrations of the PMMA solution were prepared by dissolving various amounts of PMMA in chloroform. PMMA solutions prepared were spun on to glass and IDT substrates.

Equation (2.1) is then used to calculate the thickness of the film. (by weight method)

$$\rho = \frac{M}{V} = \frac{M}{A} \times t$$

Where $\rho$ is the density of the PMMA (1.17gm/cc), $M$ is the mass of the film, $V$ is the total volume of the PMMA film which is product of area ‘A’ of the film covered and ‘t’ thickness of the PMMA film.
2.3.2. **Plasma Treatments of Conventional PMMA:**

The spin coated PMMA on copper ID structure, silicon and bare glass substrates were treated in Ar plasma in a tubular plasma system (EMITEK 1050X). The system was initially evacuated to $10^{-2}$ Torr using a rotary pump. Ar gas was then flushed for ten min before adjusting the pressure to 0.2 Torr. The power was varied between 40 to 60 Watt at the variable time of 5 to 15 minutes.

![Plasma System](image)

**Fig 2.3:** **PLASMA SYSTEM (EMITECH, K 1050X, ENGLAND)**

Fig. 2.3 shows the schematic of the system used for the experiment. This system is specially used for the surface treatment of polymers. The most important components of this system are a vacuum chamber, a vacuum pump, a high-frequency generator for plasma creation and a gas feeding system.

2.3.3 **Monomer (MMA) Distillation:**

The commercially available monomer contains an inhibitor added intentionally for preventing polymerization. This has to be removed first before the monomer could be used for polymerization. Distillation under pressure lower than the normal atmospheric pressure is most suitable method for the purification of many organic liquids. For the present work methyl methacrylate (MMA) 99.00% (from Aldrich chemical company Inc.) 86 inhibited with 10 ppm of hydroquinone monomethyl ether/4-methoxy phenol (MEHQ) is purchased.

The thermodynamic properties of MMA and its inhibitor are given below:
<table>
<thead>
<tr>
<th></th>
<th>MMA</th>
<th>MEHQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point (b.p.)</td>
<td>100 °C</td>
<td>243 °C</td>
</tr>
<tr>
<td>Melting point (m.p.)</td>
<td>-48 °C</td>
<td>55-57 °C</td>
</tr>
<tr>
<td>Molecular weight (m.w.)</td>
<td>100.12</td>
<td>124.14</td>
</tr>
</tbody>
</table>

The schematic of the distillation set up is shown in Fig-2.4. The monomer was first washed with 5% NaOH solution to remove the inhibitor such as hydroquinone and later twice with distilled water using a separating funnel to remove the un-reacted NaOH. The monomer is dried using Na₂CO₃, NaSO₄ or MgSO₄. It is again dried with CaH₂ and kept for one hour.

The distillation is carried out at a pressure of 5-10 Torr in nitrogen atmosphere using the standard procedure. The required pressure is achieved using water pump through low temperature trap. The monomer is then heated at a constant temperature of approximately 45°C throughout the experiment, measured with a mercury thermometer.

Distilled MMA is collected in a flask which is kept at low temperature in an ice-salt bath. The distilled monomer is removed and preserved at low temperature. The purity of the distilled monomer is verified using FTIR spectroscopy.

![Fig-2.4: Monomer Distillation setup](image-url)
2.3.4 Plasma Polymerization of MMA (PPMMA deposition):

The ID pattern developed by photolithography together with glass samples (for ESCA analysis) and silicon samples (for FTIR analysis) were used as substrates for plasma polymerization.

The schematic plasma polymerization set up is shown in Fig-(2.5). It consists of an inductively coupled tubular type gas flow reactor, rotary pump; RF generator, an impedance matching unit and liquid nitrogen trap [32]. The substrate holder was water cooled to maintain the substrate below room temperature. It is attached to the chrome-coated mild steel base plate. The system was evacuated using a rotary pump through a liquid nitrogen trap.

![Fig-2.5: RF Plasma Polymerization System](image)

Plate-I: Plasma Polymerization System
The liquid nitrogen trap is used to condense the un-reacted monomer which will otherwise contaminate the rotary pump oil and also the laboratory environment. The reactor is inductively coupled to a RF power supply (RF plasma products, New Jersey model–5S) which operates at a fixed frequency of 13.56 MHz (established by international agreements) with a power output in the range 0 to 555 W.

A pie type impedance matching network (Model MN–500 from RF plasma products) is used to match the impedance of the plasma to the RF generator. The facility of the forward power and reflected power measurements is also provided in this model. The actual power fed to the plasma is the difference between the forward power and the reflected power.

The RF power is fed to an inductive coil, wound on the slim portion of the reactor (Fig-2.5) through a matching unit. The inductive coil has seven turns and is made up of hollow copper tube of 6mm outer diameter, it was tapped to the fourth turn to give an inductance of 0.95 $\mu$H.

After feeding the RF power to the coil, the inductor coupled to the reactor acts as an antenna and radiates the RF power outside to an approximate distance of about 2m, which considerably influences the AC mains line and fluctuations are observed on the instrument like DC power supply or MFC’s etc. Hence any electronic instruments in the laboratory start malfunctioning. To avoid this, reactor is shielded with mild steel sheet box which is earthed electrically. The shield prevents the radiation coming out from the inductive coil. The reflected power is observed on the RF generator and the actual power coupled to the plasma is calculated by subtracting the reflected power from the input set power.

Mass flow controllers (MFC) of the accuracy of 0.1 sccm are used for the measurements of the carrier gas and the monomer flow rates. The MFC’s are equipped with bypass valve so that before starting the actual deposition the air and other impurities from the monomer reservoir can be pumped out.

Flexible teflon tubes are used to introduce the carrier gas and the monomer into the reactor, as teflon does not react with the monomer. The system pressure is measured using digital pirani gauge (Model DHPG–1025), supplied by Hind High Vacuum Co. The system is evacuated using a rotary pump (Hind High Vacuum Co.) and the pumping rate is adjusted using diaphragm valve connected between the liquid nitrogen trap and the rotary pump, this helps in setting the required system pressure during the deposition.
The glass substrates with the ID structure to test the humidity response, Si samples for FTIR analysis and plain glass substrates for thickness measurement were mounted onto water cooled substrate holder after cleaning the substrates and the reactor.(Plate-1)

Initially the reactor is evacuated to a pressure of $1 \times 10^{-2}$ Torr. After evacuating the system the gas line was evacuated [32]. The system was flushed for ten min by introducing argon at high flow rate to flush the system with argon. The argon flow rate is then reduced to get the specified experimental deposition condition. After the pressure is stabilized, argon plasma is initiated for ten min at 40 W.

The intense argon plasma further cleans the substrates. The monomer trap is filled with liquid nitrogen. The monomer is then introduced into the argon glow discharge and the gas flow rates, monomer flow rate, system pressure and the power are all adjusted to the required value. Due to the reaction of the monomer which take place in the glow discharge, as the deposition starts there is slight fluctuation in the system pressure. The deposition parameters were varied in the ranges:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure</td>
<td>0.01 mbar</td>
</tr>
<tr>
<td>Reactor Pressure (at deposition)</td>
<td>0.1 – 0.4 mbar</td>
</tr>
<tr>
<td>MMA/Ar flow rate</td>
<td>8-35 cc/min</td>
</tr>
<tr>
<td>RF Power</td>
<td>10 – 45 W</td>
</tr>
</tbody>
</table>

A large number of such experiments were carried out by varying the gas and monomer flow rates, system pressure and input power until deposition is finally observed.

### 2.4 FTIR characterization of PMMA films:

The molecular structure of the conventional plasma treated and the plasma polymerized films has been determined by Fourier Transform infrared (FTIR) spectroscopy [32]. IR measurements of the purified MMA were also taken. The films deposited on silicon substrates were used for IR analysis. IR spectroscopic technique is most widely used technique for structural characterization of polymer films. IR spectrometer from Perkin Elmer 2000 is used in transmission mode and operated between 400 and 4000 cm$^{-1}$ in a KBr medium to record the spectra. These spectra are compared with the standard IR spectrum of the MMA. The IR spectra
of MMA, PPMMA and the conventional PMMA as well as the plasma treated PMMA are analyzed. Polymer composition and the structure of PPMMA series polymer films deposited on silicon substrate are evaluated by Fourier Transform Infrared spectroscopy (FTIR).

2.5 Relative Humidity (RH) Measurement of the sensors:

The RH response of all the sensors fabricated was measured using both the continuous and step static mode. In the continuous mode the RH is changing with time where as in the step static mode the sensor is kept at constant RH for one hour each and then moved to the next RH and so on.

2.5.1 Continuous RH Response (Resistance Measurement):

The humidity cell shown in Fig-(2.6) and Plate-II was used for the characterization of the humidity sensor. It consists of a closed flask, half filled with water (Total volume 500ml). The relative humidity of the air in the enclosed system is given by equation (2.2):

\[
\% RH = \frac{e_w(T_1)}{e_w(T_2)} \times 100
\]

Where \(e_w(T_1)\) is the saturated vapor pressure of water bath at temperature \(T_1\) and \(e_w(T_2)\) is the saturated vapor pressure at temperature \(T_2\) near sensor. The RH is varied by changing the temperature of the system using salt ice mixture. Table-2.1 gives the typical saturated vapor pressure of water with corresponding temperatures.

For the Relative Humidity response of the sensor, resistance Vs RH response was recorded using the above mentioned system. The sensor is kept in the flask 2 cm above the water level with contact leads. These leads are connected to the resistance meter for resistance measurement.

The flask is then surrounded by ice salt mixture for cooling, where as for the warming up process the ice bath is simply removed. From variations in \(T_1\) and \(T_2\) the RH is calculated, the resistance is noted on the digital multimeter from Rish (Model No.-12S) and the plots of resistance Vs RH are drawn. All the measurements were repeated twice to minimize experimental errors.
### Table-2.1: Typical saturated vapor pressures of water at different temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Saturated Vapor pressure</th>
<th>Temperature °C</th>
<th>Saturated Vapor pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>-15</td>
<td>1.436</td>
<td>13</td>
<td>11.231</td>
</tr>
<tr>
<td>-14</td>
<td>1.560</td>
<td>14</td>
<td>11.987</td>
</tr>
<tr>
<td>-13</td>
<td>1.691</td>
<td>15</td>
<td>12.788</td>
</tr>
<tr>
<td>-12</td>
<td>1.834</td>
<td>16</td>
<td>13.634</td>
</tr>
<tr>
<td>-11</td>
<td>1.987</td>
<td>17</td>
<td>14.530</td>
</tr>
<tr>
<td>-10</td>
<td>2.149</td>
<td>18</td>
<td>15.477</td>
</tr>
<tr>
<td>-9</td>
<td>2.326</td>
<td>19</td>
<td>16.477</td>
</tr>
<tr>
<td>-8</td>
<td>2.514</td>
<td>20</td>
<td>17.535</td>
</tr>
<tr>
<td>-7</td>
<td>2.715</td>
<td>21</td>
<td>18.650</td>
</tr>
<tr>
<td>-6</td>
<td>2.931</td>
<td>22</td>
<td>19.827</td>
</tr>
<tr>
<td>-5</td>
<td>3.163</td>
<td>23</td>
<td>21.068</td>
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<tr>
<td>-4</td>
<td>3.410</td>
<td>24</td>
<td>22.377</td>
</tr>
<tr>
<td>-3</td>
<td>3.673</td>
<td>25</td>
<td>23.756</td>
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<tr>
<td>-2</td>
<td>3.956</td>
<td>26</td>
<td>25.209</td>
</tr>
<tr>
<td>-1</td>
<td>4.258</td>
<td>27</td>
<td>26.739</td>
</tr>
<tr>
<td>0</td>
<td>4.579</td>
<td>28</td>
<td>28.349</td>
</tr>
</tbody>
</table>
2.5.2 Static Step RH Response (Capacitance Measurement):

For the static step RH response, saturated salt solutions of five different salts were used. Borosilicate glass test tubes (diameter 1.25 in.) were initially cleaned using the procedure described earlier in section (2.3.2). The AR-grade salts were then introduced into the respective test tube using a spatula, the salts were made wet by using de-ionized water using a dropper. Care was taken to just wet the salt completely and not to dissolve the whole salt in water, thus a saturated salt solution was prepared. Table-2.2 shows the saturated salt solutions used and the respective humidities obtained over them. The test tubes were sealed using a greased rubber stopper into which wire leads were inserted.

Table-2.2: Saturated salt solutions used and the respective relative humidities obtained over them.

<table>
<thead>
<tr>
<th>Saturated Salt solution</th>
<th>% Relative Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preheated Silica gel</td>
<td>00%</td>
</tr>
<tr>
<td>LiCl</td>
<td>12%</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>33%</td>
</tr>
<tr>
<td>Mg (NO₃)₂</td>
<td>53%</td>
</tr>
<tr>
<td>NaCl</td>
<td>75%</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>97%</td>
</tr>
</tbody>
</table>
The sensors were initially placed in silica gel for 1 hr, and the capacitance was recorded. Then it was transferred to each constant RH cell with increasing RH from 0%, 12 %RH to 92%. The sensors were kept in each cell at constant RH for one hour before the capacitance was recorded. The readings were repeated for decreasing in RH i.e. from 92% RH to 0% in a similar fashion. The measurements were repeated twice to minimize errors.

2.5.3 Response and recovery Time of the Sensor:

The response time of spin coated, plasma treated and plasma polymerized sensors was measured by first keeping the sensor in dry environment (silica gel) for 24 hrs. Its dry capacitance/resistance was then recorded. The sensor element was then immediately transferred in a static RH environment namely 75% or 92%. The change in capacitance/resistance over time was recorded after every one sec till the capacitance/resistance showed saturation. The graph of capacitance/resistance Vs time was plotted. From this graph the response time was calculated in the linear portion of the curve between 10% and 90 %RH.

The recovery time of plasma treated and plasma polymerized sensors was measured by first keeping the sensor in humid environment (K$_2$SO$_4$) for 1 hour. Its humid capacitance/resistance was then recorded. The sensor element was then immediately transferred in a static RH environment namely 12% or 0%. The change in capacitance/resistance over time was recorded after every one sec till the capacitance/resistance showed saturation. The graph of
capacitance/resistance Vs time was plotted. From this graph the recovery time was calculated in the linear portion of the curve between 90% and 10 %RH.

2.6 Optical response of PMMA:

The PMMA solution (Concentration 0.1gm in 10 ml of chloroform) was then used to form the films of PMMA by drop casting (5µL of solution by a micropipette) on the borosilicate glass substrate having fixed area of 1cm×1cm. Drop was spread on the substrate neatly which were used as samples. The thicknesses of the films were varied by changing number of drops of PMMA solution. The thicknesses of the films were measured by using gravimetric method.

A simple optical method was used to test the prepared films for their sensitivity towards humidity. Closed humidity system for testing the humidity responses of the films was fabricated as shown in Fig. 2.7. It consists of a closed glass chamber (volume: 6 L), with a neck for inserting a sample under test and a probe of the standard Vaisala humidity meter (humidity range: 0–100% RH with an accuracy of 1–5% RH for different humidity ranges). The chamber was kept on an aluminum plate and was sealed from outside by modeling clay to make the system air tight. The relative humidity was created inside the chamber by keeping hot water in the beaker and simultaneously monitoring the humidity to get maximum(85%)RH at room temperature (30–35°C) as measured by the standard Vaisala humidity meter. After achieving 85% RH the beaker was removed. The 85% RH was kept for 5 min. The chamber was gently lifted and the saturated vapors were wiped by tissue papers and the chamber was kept at its original position. Humidity was decreased by putting dehumidifying material like phosphorous pentoxide (P₂O₅) in an appropriate amount in a pettry dish. While humidifying and dehumidifying the chamber, the 2–5°C change in the temperature was observed.

A He–Ne laser beam, incident perpendicular to the plane of the film, is allowed to pass through the sample (films) and the transmitted output is measured using a simple photovoltaic detector. The samples were mounted in the chamber and were exposed to the highest humidity. The related output in the form of voltage was measured by Digital Multimeter (DMM) (Agilent U1241A).
Keeping dehumidifying material (Thomas Baker’s P₂O₅ LR grade) in the chamber, relative humidity was decreased to the lowest value and related voltage was also noted. The change in relative humidity is related to the change in the output voltage of the sample. Normalized output with respect to the lowest relative humidity is plotted. Output is normalized with respect to voltage at lower humidity i.e.

\[
\text{% Normalized Output} = \left( \frac{V_{lh} - V_{hh}}{V_{lh}} \right) \times 100
\]

Where \( V_{lh} \) is output voltage at low humidity and \( V_{hh} \) is output voltage at high humidity.

The sensitivity is defined as the change in transmitted output (mV) per unit change in RH%, i.e. \( \delta \text{ (mV)} / \delta \text{ (RH%)} \) [6]. As there are four samples (one, two, three and four drop) having different thicknesses, sensitivity is calculated for each sample.

We noted optical response of drop casted as well as spin coated PMMA samples.

**Measurement of moisture in the samples**

For the measurement of moisture, the samples were exposed to 100% RH for around 10 min. and then immediately weighted (\(W_x\)) on electronic balance (Citizen CX165) Then these samples are vacuum dried and weighted again at room humidity (35%RH). The percentage moisture content is calculated using following equation [19]

\[
\text{Moisture(\%)} = \left( \frac{W_x - W_0}{W_0} \right)
\]