Chapter II

Experimental Techniques
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, plasma polymerization, plasma treatment, structural characterization by FTIR, XPS, Contact angle measurements and the response of the material to relative humidity.

2.2 Sensor Fabrication:

For the sensor fabrication an interdigitated capacitive (IDC) type sensor structure is 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 this article.
2.2.1 Fabrication of ID structure:

Glass is selected as a substrate in all these experiments, it being non sensitive to humidity. Chromium is chosen as the electrode material since it has good adhesion to glass and inertness towards active gases as well as moisture. For the fabrication of chromium ID structure on glass, chromium was first deposited on to glass substrate, followed by mask preparation and photolithography.

2.2.1.1 Cleaning of Glass Substrates:

Prior to chromium deposition on glass substrates, the glass substrates (boroslicate 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 samples were then dried using nitrogen gas.

2.2.1.2 Chromium Deposition On Glass Substrates:

For the deposition of chromium initially sputtering system was used as it provides good adhesion compared to other deposition processes. Later however, the physical vapor deposition (PVD) system had to be used.

(a) Sputter deposition:

Fig-(2.2) shows the sputtering system used in the present experiments. The system was available in our laboratory. Its long length allowed us to deposit chromium on to a large number of substrates simultaneously. Borosilicate glass samples were used as substrates which were cleaned just before deposition as mentioned in 2.1.1.1 above. The reactor was loaded with the properly cleaned glass substrates and evacuated to pressure of $2 \times 10^{-5}$ Torr. Argon gas is then filled in the reactor till the vacuum reaches to about 0.5 to 1 Torr. This required pressure is achieved by adjusting the argon flow, using a needle valve. Negative high voltage is applied to the chromium cathode and the substrates were kept on the anode at ground potential. A long target deposited with thick chromium layer of the order of 10 $\mu$m by electroplating is used in this case.
In order to get opaque pinhole free and uniform adherent chromium films sputtering parameters such as gas pressure and voltage were varied between 0.3 Torr to 1 Torr and 1000 to 1200 Volts respectively. The sputter deposition was always carried out for one hour. Large number of experiments had to be carried out until adherent pinhole free deposition took place. The process parameters at which such chromium films were obtained were pressure < 0.5 Torr, voltage = 1200 Volts and the current 150 mA.

The film adhesion was tested by scratching the film with a steel pin. The films did not scratch off. The thickness of the deposited films was measured using tally step method and was found to be around 2000 Å. When observed through the Scanning Electron Microscope (SEM) very few pin holes were observed.

(b) Physical vapor deposition:

Another method used for the deposition of chromium was physical vapor deposition (PVD). The cleaned glass substrates were mounted on to the substrate holder of the PVD system. The thermal evaporation was carried out using a coating unit supplied by Hind High Vacuum Co. Ltd. (Model No.12A 4). The substrates were heated to 200 °C using a radiation heater held above the substrates for good adhesion of chromium to the glass substrate. The reactor was evacuated to a pressure of $10^{-5}$-$10^{-6}$ Torr
after which chromium was evaporated from the conical shaped tungsten filament. Fig-(2.3) and Plate-I shows the schematic of the PVD system used.

**Fig-2.3: The Physical Vapor Deposition (PVD) System**

Plate-I: Physical Vapor Deposition (PVD) system
2.2.2.1 Monomer (MMA) Distillation:

The commercially available monomer contains quinone inhibitor added intentionally for preventing polymerization. This has to be removed first before the monomer could be used for polymerization. The purification is done by fractional distillation under reduced pressure. Distillation under pressure lower than the normal atmospheric pressure is most suitable method for the purification of many organic liquids. The experimental setup and the procedure are discussed here. In this work methyl methacrylate (MMA) is used as a base monomer which is commercially available.

The thermodynamic properties of MMA and its inhibitor are given below:

<table>
<thead>
<tr>
<th></th>
<th>MMA</th>
<th>MEHQ</th>
</tr>
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<tr>
<td>Boiling point (b.p) at 760 mm of Hg</td>
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<td>243 °C</td>
</tr>
<tr>
<td>Melting point (m.p.)</td>
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<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 an hour. The prepared monomer is then distilled from CaH2 in nitrogen atmosphere at reduced pressure.
temperature dependent. The development time was varied between 0.5 to 4 min at room temperature.

4. Etching of chromium:

Etching involves the selective patterning or etching away of the metal. For etching of chromium, the etchant used was ceric ammonium nitrate (CAN): A solution of ceric ammonium nitrate was prepared by dissolving 20.62 grams of CAN in 100 ml of DI water with 4.5ml of acetic acid.

5. Stripping of resist:

Stripping or the removal of the resist is carried out without damaging the substrate. For negative resist organic strippers like trichloroethylene and monochlorobenzene are normally used but, acetone also works equally well.

For proper pattern transfer, all the above parameters were varied a number of times until it was found that for exact ID pattern transfers giving the designed dimensions onto chromium are obtained. The following parameters were found to be most suitable:

- Resist thickness – 1500–2000 µm
- Resist spinning speed – 3000-4000 rpm
- Resist spinning time – 1.5 min
- UV Exposure time – 6 min
- Development time – 2 min
- Etching time – 3-4 min (depending on chromium thickness)

More than seventy such patterns were fabricated which were required for further experiments. The capacitance in air of all the samples was measured and was found to be between 11-12 pF.

2.2.2 Deposition of the Sensing Material:

After the ID pattern was transferred onto chromium the sensing materials i.e. plasma polymerized MMA and plasma treated PMMA have to be deposited between the inter digits.
2.2.2.1 Monomer (MMA) Distillation:

The commercially available monomer contains quinone inhibitor added intentionally for preventing polymerization. This has to be removed first before the monomer could be used for polymerization. The purification is done by fractional distillation under reduced pressure. Distillation under pressure lower than the normal atmospheric pressure is most suitable method for the purification of many organic liquids. The experimental setup and the procedure are discussed here. In this work methyl methacrylate (MMA) is used as a base monomer which is commercially available.

The thermodynamic properties of MMA and its inhibitor are given below:

Methyl methacrylate (MMA) 99.00% (from Aldrich chemical company Inc.) 86 inhibited with 10 ppm of hydroquinone monomethyl ether/4-methoxy phenol (MEHQ).

<table>
<thead>
<tr>
<th></th>
<th>MMA</th>
<th>MEHQ</th>
</tr>
</thead>
<tbody>
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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 an hour. The prepared monomer is then distilled from CaH₂ in nitrogen atmosphere at reduced pressure.
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 46 °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.

2.2.2.2 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 plasma polymerization set up is shown in Fig-(2.5) and Plate (II). It consists of an inductively coupled tabular type gas flow reactor, rotary pump, RF generator, an impedance matching unit and liquid nitrogen trap. 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.

![RF Plasma Polymerization System](image)

**Fig-2.5: RF 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 the 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 μH.

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 of 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 XPS analysis were mounted onto water cooled substrate holder after cleaning the substrates and the reactor.
Initially the reactor is evacuated to a pressure of $1 \times 10^{-2}$ Torr. After evacuating the system the gas line was evacuated and the monomer was degassed by pumping and thawing technique \(^6\). 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:

- Reactor Pressure: 0.1 – 0.4 Torr
- MMA/Ar flow rate: 8-35 cc/min
- RF Power: 20 – 65 W

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.

### 2.2.2.3 Plasma Treatments of Conventional PMMA:

For the plasma treatment of the PMMA by argon and nitrogen plasmas, 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. As the thickness of the chromium ID is about 2000 Å the spin coated films had to be about the same thickness.

To obtain this thickness several experiments were carried out. Different concentrations of the PMMA solution were prepared by dissolving various amounts of PMMA in chloroform. These solutions were spun on to glass cover slips which were
initially weighed. The weight of the cover slip with the film was again recorded and from this the mass of the film was calculated.

Equation (2.1) is then used to calculate the thickness of the film:

\[
\rho = \frac{M}{V} = \frac{M}{A \times t} \quad \text{(2.1)}
\]

Where \( \rho \) is the density of the PMMA, \( M \) is the mass of the film, \( V \) is the total volume of the PMMA film which is equal to the area \( A \) of the film covered into 't' thickness of the PMMA film. From the area of the film covered, density of PMMA 2.6 g/cc and the mass of the film the thickness was calculated. It was observed that to obtain a thickness of 2000 Å, 2.5 grams of PMMA had to be dissolved in 4 cc of chloroform. This concentration was then used to spin coat all the chromium ID structures with PMMA solution to deposit the PMMA between the ID fingers. The spinning speed used was 3000-4000 rpm.

All the plasma treatments were carried out in a parallel plate DC tubular type of a plasma reactor. Fig-(2.6) and Plate-III shows the schematic of the system used for this experiment.

![DC plasma treatment system](image)

**Fig-2.6: DC plasma treatment system**
The spin coated PMMA on chromium ID structure, silicon and bare glass substrates were mounted on the lower electrode of the parallel plate for further characterizations. The system was evacuated to $10^{-2}$ Torr using a rotary pump. Ar or N\textsubscript{2} gas was then flushed for ten min before adjusting the pressure to 0.2 Torr. DC plasma was then created using a DC power supply. The current and voltages were adjusted until the required power was obtained. The power was varied between 5 to 40 Watt at a constant time of 5 min. The input power was calculated from the input voltage and current. Similar experiments were carried out by varying the treatment time from 1 to 15 min at a constant power of 5 Watt in both argon and nitrogen plasmas.

2.2.3 Dissolution Experiments of PPMMA Films:

The solubility test of the deposited films in Isopropyl alcohol (IPA) and Toluene was carried out by submerging the plasma polymerized films with the substrates in a petri dish; the dissolution time of films deposited under various conditions was recorded in min.
2.2.4 Sensing Device:

For RH measurements, the sensor i.e. the plasma polymerized films and plasma treated films on chromium ID structure on glass, were properly mounted and fixed on to a support with araldite. Thin single strand copper wire was pasted to both the arms of the IDC using silver paste for contact. The other end of the wire was soldered on to a PCB board from which thick single strand copper acted as a leads. Small crocodile clips were used to hold the leads securely which were in turn attached to the capacitance meter. Care was also taken to keep the distance between the attached wires constant. Plate-IV shows the photograph of the steps in the sensing device fabrication: (a) initial glass substrate, (b) Cr deposition by sputtering, (c) ID mask used, (d) IDC mass pattern transferred onto chromium, (e) The polymer filled into the interdigits of the chromium electrodes by plasma polymerization or spin coating, (f) final sensing device

Plate-IV: Steps involved in the fabrication of the sensor:
(a) Glass substrate, (b) Chromium deposition, (c) IDC mask, (d) IDC mass pattern transferred onto chromium, (e) The polymer filled into the interdigits of the chromium electrodes by plasma polymerization or spin coating, (f) final sensing device
2.3 Humidity Response of the PPMMA and Plasma Treated PMMA:

The RH response of all the sensors fabricated was measured using both the continuous and step static mode. In the static 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.

2.3.1 Static Continuous RH Response:

The humidity cell shown in Fig-(2.7) and Plate-V 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):

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

(2.2)

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, capacitance 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 capacitance meter for capacitance 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. For variations in \(T_1\) and \(T_2\) the RH is calculated, the capacitance is noted on the digital capacitance meter from Testronix (Model No.-57) and the plots of capacitance Vs RH are drawn. All the measurements were repeated twice to minimize experimental errors.
Fig-2.7: RH Measurement apparatus

Plate-V: Continuous RH response measurement set up
Table 2.1: Typical saturated vapor pressures of water at different temperatures

<table>
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<tr>
<th>Temperature °C</th>
<th>Saturated Vapor pressure</th>
<th>Temperature °C</th>
<th>Saturated Vapor pressure</th>
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2.3.2 Static Step RH Response:

For the static step RH response, saturated salt solutions of five different salts were used. Borosil glass test tubes (diameter 1.25 in.) were initially cleaned using the procedure described earlier in article (2.1.1.1). 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. The test tubes were sealed using a greased rubber stopper into which wire leads were inserted. Table-2.2 shows the saturated salt solutions used and the respective humidities obtained over them. Plate-VI shows the apparatus used for this purpose.

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>KNO₃</td>
<td>92%</td>
</tr>
</tbody>
</table>
The sensors were initially placed in silica gel for 1 hr, 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.

2.3.3 Response Time of the Sensor:

The response time of a typical plasma treated sensor (samples “I” and “Q”) was measured by first keeping the sensor in a dry environment (silica gel) for 24 hrs its dry capacitance was then recorded. The sensor element was then immediately transferred in a static RH environment namely 75% and 92%. The change in capacitance over time was recorded after every 30 sec till the capacitance showed saturation. The graph of capacitance Vs time was plotted. From this graph the response time was calculated in the linear portion of the curve between 10% and 90 %RH.
2.4 Structural Characterization Techniques:

The molecular structure of the conventional and the plasma polymerized films has been determined by Fourier Transform infrared (FTIR) spectroscopy and the elemental analysis is done by X-ray photoelectron spectroscopy (XPS). IR measurements of the purified MMA were also taken. The films deposited on silicon substrates were used for IR analysis and those deposited on silicon wafers/glass substrates were used for XPS analysis.

Cleaning of the silicon samples:

The silicon wafer is used as a substrate for sensing material deposition for characterization purpose. The wafer was cut into $1\text{cm}^2$ pieces using a diamond cutter. The samples then were cleaned with neutral soap solution (labogen) then rinsed with deionized water and finally ultrasonically cleaned in methanol, they were later dried in nitrogen gas.

2.4.1 Infrared Analysis:

The most widely used spectroscopic technique for determining the plasma polymerized films has been the (IR) spectroscopy which exhibits high sensitivity of particular feature. IR spectrometer from Perkin Elmer 783 is used in transmission mode 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). The spectra are recorded in transmission mode using Perkin-Elmer double-beam spectrophotometer having $2\text{ cm}^{-1}$ resolution.

2.4.2 XPS Analysis:

The compositional, structural and elemental analysis is done by X-ray photoelectron spectroscopy (XPS). All the photoemission measurements are carried out in Vacuum Generator ESCA LAB MKII, a commercial system supplied by V.G Scientific, England. Experiments are carried out in the base pressure of $10^{-9}$ Torr. Spectra are recorded using AlK$_\alpha$ exciting radiation (photon energy 1486.6 eV). The maximum
resolution achievable is 0.9 eV. The X-ray tube was operated at 10 kV and 20 mA. As the X-ray source was not monochromatic, overall resolution, obtained using a concentric hemispherical analyzer, was 1.0 eV. It was operated 20 eV pass energy. Gold is used as an external reference with 4f\(_{7/2}\) at 84 eV ±0.2 eV. To avoid the signal from sample holder, one cm square sample is used.

2.4.3 Contact Angle Measurements:

Contact angle measurement is a simplified method of characterizing adhesion and wetting properties \(^{87}\) like:

- Surface and interfacial tension
- Surface and material modification
- Contamination detection and effects

Though there are various methods of measuring contact angle the direct method of measurement of contact angle is done normally by taking a photograph of the sessile drop resting on the solid and then measuring the angle from the print. In the present work, the contact angle is measured directly by an NRL contact angle goniometer telemicroscope (comparator microscope fitted with a goniometer scale).

A drop of liquid resting on the surface of the liquid is shown in Fig-(2.8) forming an angle \(\theta\) with the surface. The liquid may be considered to be in equilibrium by balancing the three forces involved, namely, the interfacial tension between solid and liquid, \(\gamma_{sl}\), that between solid and vapor, \(\gamma_{sv}\), and between the liquid and the vapor \(\gamma_{lv}\).

![Fig-2.8: Sessile drop on surface](image)
The angle of contact is actually the angle between the tangent plane to the surface of the liquid and the tangent plane to the surface of the solid at any point along their line of contact.

\[ \gamma_{sv} = \gamma_s \cos \theta + \gamma_v \]  
\[ \text{(Young's Equation)} \]

The contact angles were obtained by sessile drop technique on a Ramé-Hart contact angle goniometer Model NRL100-00-200. The instrument is a small bench type device incorporating an internal protractor read out calibrated in 1 degree increments. Its low power microscope produces a sharply defined image of the sessile drop specimen which is observed.

The precision specimen stage permits the specimen to be easily aligned using the two, independently rotatable crosshairs within the microscope and is calibrated both horizontal as well as vertical axes in 0.02 mm divisions. This allows the physical measurements of the drop to be accurately determined.

The measurement of contact angle was done by keeping the substrate on the specimen stage and placing a sessile drop of double distilled deionized water on to its surface. The drop was then focused through the microscope and the vertical axis was rotated so as to form a tangent at the top of the base. The contact angel is read directly from the internal protractor readout. The contact angle was measured at both end points of the drop and the average of the two was taken. Such contact angels were taken at three different parts of the sample and their average values have been reported. From the average contact angles the work of adhesion was calculated using the equation:

\[ W_a = \gamma_L (1 + \cos \theta) \]  
\[ \text{(2.4)} \]

Where, \( W_a \) is the work of adhesion, \( \gamma_L \) the surface tension of water, \( \theta \) the angle of contact.

**2.4.4 Dielectric Loss Measurements of Argon Plasma Treated PMMA:**

The argon plasma treated PMMA films on chromium ID were further used for their dielectric response namely dielectric loss. The dielectric response of these samples was recorded using an LCR meter bridge HP 4263 B.
The dielectric response was measured at 100 Hz. For each plasma treated sample as well as untreated PMMA, the dielectric response was measured and the temperature of the sample was varied using a heater. The response for each constant frequency was taken at temperatures: 27, 45, 65, 75, 85, 95 °C.

Graphs of variations of tanδ with temperature were plotted for PMMA and plasma treated PMMA.

2.4.5 H₂O Diffusion Studies of Plasma Treated Samples:

To study the diffusion of H₂O into the polymer, the plasma treated samples were initially kept in 0%RH for an hour after which they were immediately transferred to higher %RH environments—in 75% and 92% static RH cells. The change in capacitance was measured with time intervals of 30 sec until saturation was reached.

A graph of normalized delta capacitance (dC) Vs vt/2 in sec is plotted. From the normalized capacitance signal for fixed humidity the diffusion coefficient D is calculated using Fick's Law.