Chapter III

Results and Discussion on humidity sensing characteristics

Results on humidity sensing characteristics of spin coated, plasma treated and plasma polymerized PMMA films are described in this chapter and discussed. Further they are compared amongst themselves and with the ones available in the literature.

3.1: Spin Coated PMMA as humidity sensor- Results and Discussion

3.1.1 Introduction

The process of applying a solution to a horizontal rotating disc, resulting in ejection and evaporation of the solvent and leaving a liquid or solid film, is called spin coating. Spin coating is a unique technique in the sense that it is possible to apply a highly uniform film to a planar substrate over a large area (30 cm) with a highly controllable and reproducible film thickness. The spin-coating technique applies to inorganic, organic and mixtures of inorganic/organic solution.

Because of its ability to produce uniform layers, transparency in visible wavelengths and its suitable glass transition temperature, PMMA (Poly (methyl methacrylate)) is used as host in many opto-electronic applications. In thin film humidity sensing applications, achieving the required thickness with desirable surface quality is very important. To produce a coating with such thickness, dilute solutions of polymer are necessary. Generally, thickness of layer in this method is dependent on spin speed, primary concentration, viscosity of solution and solvent vaporizability [1, 2]. The nature of this dependency varies across different materials and solutions.

Depositing a viscous fluid on a horizontal rotating disc produces a uniform liquid film. During deposition the disc should either be static or be rotating at a low spin speed, where after the disc is rapidly accelerated to a high spin speed. The adhesive forces at the liquid/substrate interface and the centrifugal forces acting on the rotating liquid result in strong sheering of the liquid which causes a radial flow in which most of the polymer solution is rapidly ejected from the disc. This process combined with subsequent evaporation of the liquid causes the thickness of the remaining liquid film to decrease. For a solution, e.g. a polymer solution, the evaporation process causes the polymer concentration to increase (and thus the viscosity) at the liquid/vapor interface, i.e. a concentration gradient is formed through the liquid film, which, after evaporation of most of the remaining solvent, consequently results in the formation of a uniform practically solid polymer film.
It is thus known that spin speed and solution concentration significantly affect the film thickness, while the amount of solution initially deposited on the disc, the rate at which it is deposited, the history of rotational acceleration prior to the final acceleration, and the total spin time have limited or no effects.

3.1.2: Sample preparation by spin-coating process

Spin coating of PMMA on to silicon substrate was carried out at various conditions. The concentrations of PMMA were taken as 0.1g, 0.2g and 0.3g / 10cc of CHCl₃. The baking temperature of the sample after spinning was kept at 50°C. This temperature range was selected as the T_g of PMMA is 105°C. Above this temperature PMMA may degrade. Moreover baking of the photoresists, which are basically polymer/resins is also done in the similar temperature range. The baking time was kept at 20 min. At this time the film becomes completely dry and nonsticky. Due to baking the film becomes dry and its adhesion with substrates also get improved. The spinning was carried out at different spin speed of 500, 1000 and 1500 rpm for a constant time of 1 min. The FTIR spectra were taken on one sample for each condition.

As described above, total 27 samples were prepared. The baking temperature was 60 °C and baking time was 20 minutes. The spin speed, concentration and obtained thicknesses are tabulated in table 1 below.

### Table-3.1: Thickness (µm) variation at different Spin speed and PMMA concentration.

<table>
<thead>
<tr>
<th>Conc. (gm)</th>
<th>Spin speed (rpm)</th>
<th>0.1</th>
<th>0.1</th>
<th>0.1</th>
<th>0.2</th>
<th>0.2</th>
<th>0.2</th>
<th>0.3</th>
<th>0.3</th>
<th>0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500</td>
<td>5.25</td>
<td>5.19</td>
<td>5.27</td>
<td>5.70</td>
<td>5.64</td>
<td>5.72</td>
<td>5.98</td>
<td>6.09</td>
<td>6.11</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>3.40</td>
<td>3.22</td>
<td>3.30</td>
<td>3.61</td>
<td>3.70</td>
<td>3.69</td>
<td>4.36</td>
<td>4.40</td>
<td>4.47</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>2.84</td>
<td>2.79</td>
<td>2.80</td>
<td>3.10</td>
<td>3.01</td>
<td>3.08</td>
<td>3.28</td>
<td>3.34</td>
<td>3.29</td>
</tr>
</tbody>
</table>

As can be seen from the table for particular concentration the thickness of the film decreases with increase in the spin speed. This is indicated in the following table 3.2 and Fig 3.1.
Table-3.2 Thickness variation w.r.t. speed and concentration.

<table>
<thead>
<tr>
<th>Speed (RPM)</th>
<th>Average Thickness(μm)</th>
<th>Concentration(gm)</th>
<th>Fig-3.1-Schematic of the relation between film thickness, speed and concentration in the spin-coating process.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>500</td>
<td>5.23</td>
<td>5.7</td>
<td>6.09</td>
</tr>
<tr>
<td>1000</td>
<td>3.22</td>
<td>3.61</td>
<td>4.4</td>
</tr>
<tr>
<td>1500</td>
<td>2.85</td>
<td>3.01</td>
<td>3.29</td>
</tr>
</tbody>
</table>

For particular spin speed the thickness is larger for larger concentration (larger viscosity). These results are as per expectations [2-6]. It can also be seen that for particular concentration the change in the thickness is not greater than 5%. This indicates the reproducibility of the results. The thicknesses obtained are in the range of 2.79μm to 6.11 μm.

3.1.3: FTIR Characterization of the spin coated films:

In order to confirm the deposition of PMMA, FTIR absorption spectra of the deposited films on silicon substrate was taken (Fig.3.2).
Fig.3.2 shows the representative IR spectra of the untreated PMMA films spin coated by 500, 1000, 1500 RPM on to silicon substrates. The peak values observed at 2995, 2946, 1731, 1447, 1240, 1149, 986, 610 cm$^{-1}$ are attributed to CH$_2$ asymmetric stretch, CH$_2$ symmetric stretch, carbonyl group (C=O), C=CH$_3$, C-O, CH bend in ester group, O-CH$_3$ rocking and silicon respectively. These peaks match with the standard reported FTIR spectra of PMMA [7, 8] indicating confirmation of PMMA films. A broad –OH feature in the spectrum between 3600-3900 cm$^{-1}$ is due to chemisorbed H$_2$O [8]. This shows all the expected peaks of PMMA confirming the material.

3.1.4: SEM of spin coated film:

Scanning electron microscopy was carried on all the spin coated samples. The typical micrograph is shown in fig.3.3

The films coated with 1000 and 1500 RPM of 0.1, 0.2 and 0.3gm concentration showed smooth, uniform surface with no cracks or micro-pores at all magnifications and also at high resolutions hence they were not photographed.

Typical SEM photographs of the film spin coated at 500 RPM and the other at 1000RPM with the concentration of 0.3gm on silicon substrate are shown in Fig.3.3(a and b) respectively. The topography is different in the two films.

Fig-3.3: SEM of spin coated film.
3.1.5: Humidity Response of the spin coated films:

Humidity response of the films was initially measured in terms of change in resistance. It was observed that the resistance value was in GΩ and the readings were not stable. Secondly it was also observed that change in resistance with humidity was very small, of the order of KΩ and therefore cannot be measured accurately. Therefore it was decided to use capacitance method. Next the voltage-divider or Wheatstone-bridge circuit is typically used for most resistive sensor applications. It is reported by Story et. al. [9] that the linearity of the humidity response depends on the relative values of the film resistance and external resistance selected. For small values of external resistances in relation with the film resistance the humidity response is nonlinear and for comparable values the relation is linear. The resistances of the films in the present work are found to be very high. Therefore high value of external resistance is required which will pose problems in stability of the readings. This circuit characteristic limits the ability of a resistive sensor to provide a linear response with high sensitivity at low RH levels, but can provide increased sensitivity at higher RH levels. This also prompted the use of capacitive measurements.

Films of various thicknesses in the range of 2.79μm to 6.11 μm were used for humidity sensing. Humidity response of the films in terms of capacitance was initially measured using continuous step method. No repeatable results were obtained. This may be because of the slow response of PMMA to comparatively fast variation of humidity. Further experiments were therefore carried out using step static method.

To take the readings of capacitance with changing humidity LCR meter (Agilent 4284A) was used. Here one other parameter was introduced and that was frequency. Readings of capacitance as a function of frequency (from 300Hz to 1MHz) at different humidity levels for all the films were taken. The responses were similar. A typical response for thickness 5.25μm is plotted in Fig. 3.4. It is observed that the capacitance is almost constant over the given frequency range except at 500Hz and 1MHz. At these two frequencies high capacitance value is observed. The reason of these high values is yet to be known. Therefore these frequencies are not used in further measurements.
Fig-3.4: Capacitance Vs frequency variation for one sample.

It is also observed that the capacitance increases with humidity and the change in capacitance occurred for each frequency (including 500Hz and 1MHz) is not greater than 3pF. Humidity response is studied, at typical frequency of 5000Hz.

Fig-3.5: Capacitance Vs Humidity variation for different thicknesses.

Humidity response of the films of different thicknesses measured at frequency of 5000Hz is shown in Fig.3.5. It shows that as the thickness of film increases, its capacitance value also increases. This is as expected because the value of the capacitance is directly proportional to the cross-sectional area of the dielectric film. It may be noted that the electrodes of IDT are 33micron thick and inter electrode distance is 0.5mm. Further the PMMA film thickness varies from 2.85 to 6.11micron.
Therefore it is possible that the electric field between the electrodes is entirely through film. So films can work here as a dielectric material. So depending upon thickness we got the variations in the capacitance values [9].

Further the response of all the films of different thicknesses is linear. It may be noted that capacitive-type humidity sensors rely on a change in permittivity ($\varepsilon$) of a ceramic or polymer dielectric with relative humidity. PMMA adsors water. Water has permittivity of $\sim 80$ and therefore adsorption of water is increasing the permittivity of PMMA which is 2.6. Since amount of water adsorbed increases with increase in humidity and therefore the capacitance increases.

If thickness Vs sensitivity (slope) graph Fig.3.6 of these values is plotted, it shows a random variation. This may be attributed to the variation of the humidity affected thickness of the films. Since PMMA is hydrophobic whole of the thickness of the film may not absorb humidity. How much thickness will get affected is unpredictable.

![Graph](image)

**Fig-3.6: Thickness Vs sensitivity (slope) graph**

The sensitivity of high thickness film is greater than films having low thickness. So graph indicates some variations accordingly.

**3.1.6: Response and recovery time of the films:**

Response and recovery time of spin coated film having 6.11 μm thickness was taken. It was approximately 10 minutes and recovery time of 12 minutes which were better than reported value of 7-14 min [10] for the plasma treated films and 15 min [11] for different humidity values.

In spin coated films, thickness of the film is of the order of some microns. The adsorbed water do not get into the film, but it remains on the surface only. So the change in response time and recovery time is attributed to surface phenomena.
3.1.7 **Hysteresis of spin coated films:**

Hysteresis is defined as the maximum difference in the response curves taken while increasing and decreasing the variable parameter, at the same value of parameter. The hysteresis curves (capacitance versus humidity) for 6.11µm thickness film is shown in fig.3.7. The hysteresis is found to be 1% for all RH values. For other films also hysteresis of same order was observed. The hysteresis in the response at lower RH is a result of slow desorption of the water from the surface of PMMA. At higher humidity, the condensation occurs and forms a cluster over the surface of the film, which attributes to hysteresis [10].

![Fig-3.7: Response and recovery time of film.](image)

![Fig-3.8: Hysteresis result for 6.11µm thickness film.](image)

The sorption mechanism can be understood by considering a dry sample placed in certain humidity, and then the zone which is immediately adjacent to the surface takes up water both by filling of micro-voids and by a process of accumulation of water on the surface which results in small clusters on the surface. The accumulation continues to contribute to the uptake of water as a result there is
acceleration in the rate of sorption which continues until the accumulation in the surface zone of the samples reaches an equilibrium value. Thereafter a constant rate of sorption is achieved [12]. The opposite will be the case in case of de-sorption.

3.2: Plasma treated PMMA as humidity sensor- Results and Discussion:

3.2.1: Introduction:

The hydrophilicity of polymers is one of the key factors that determine the surface properties of polymeric materials. It controls various properties of polymers, including wettability, adhesion, colorability, and anti-electrostaticity. Depending on the situation, sometimes more hydrophilicity or hydrophobicity of a polymer surface is desired. For modification of the surface properties of a polymer, a number of methods have been developed. Physical and chemical modifications are two main methods. The physical modifications include plasma, [13,14] corona, [15,16] flame [17] and ion beam treatments [18] while the chemical modifications comprise chemical reaction and wet treatment.[19,20]

As is observed from literature survey, surface modification of polymer surface is known to increase the wettability and surface energy of the polymer surface [21, 22]. It is thought that this technique may be able to give higher sensitivity and better response and recovery time. Secondly, as adsorption of humidity is a surface phenomenon and plasma treatment for a few minutes can easily change the surface structure, so the surface of the PMMA films is modified by plasma treatment and its effect is studied. For this purpose, Emitech K1050X Plasma Etcher/Asher/Cleaner system was used. Argon gas was introduced in the system. The flow of argon gas was 20sccm. PMMA solution of 0.1 concentrations was taken. Plasma treatment was done with the power of 20, 30 and 40watt for 2, 5 and 8 min. The system pressure was kept constant at 0.2 mbar. Power greater than 40 W and time larger than 8 min was not used as this lead to etching of the samples.

3.2.2: The plasma treatment process

Spin coating of PMMA on to IDT, glass and silicon substrates was carried out as stated in section 3.1.2. The concentration of PMMA used in the experiments was 0.1 g/10 c.c. CHCl₃. The spinning was carried out at the specific spin speed of 500 rpm for a constant time of 30 second. The samples prepared were plasma treated as explained in section 2.3.2 (check section number). The FTIR spectra were taken on one silicon sample for each condition.
3.2.3: Characterization of the plasma treated films:

3.2.3.1 FTIR analysis:

The IR spectra of the untreated PMMA film spin coated on to silicon substrates is given a discussed in detail in section 3.1.3.

Fig-3.9, 3.10 & 3.11 show the FTIR absorption spectrum of argon plasma treated samples on silicon with power variations (20, 30, 40 watts) and time variation (2, 5, 8 min.) respectively. Peaks typical of PMMA shown in Table-1 are observed. In addition some new peaks are seen to be present and/or the intensity of the old peaks is observed to have changed.

![Fig-3.9: FTIR of samples plasma treated at 20 watt for different time durations.](image1)

![Fig-3.10: FTIR of samples plasma treated at 30 watt for different time durations.](image2)
Fig-3.11: FTIR of samples plasma treated at 40 watt for different time durations

The band due to ester C-O stretching mode at 1150 cm\(^{-1}\) is broad in modified samples which is characteristic of cross linked polymer system [23,24]. Comparison of the absorption peaks seen in the region between 3600-3900 cm\(^{-1}\) (attributed to -OH feature) shows newly formed and/or increased –OH functionality’s after treatment which may be responsible for increase in the hydrophilic properties of the top surface[25]. The OH functionality varied from sample to sample suggests variation in the hydrophilic character of the topmost surface due to argon plasma treatment. For samples treated at a constant power at 40 W with time variation from 2 to 8 min are substantially reduced and not distinct(sentence incomplete what has reduced is not clear). For all the samples (except sample treated at 30 watt for 2 min.) the carbonyl and the ester functionality’s were visible and there was no notable shift in the peaks positions of C=O at 1730 cm\(^{-1}\) and C-O at 1149 cm\(^{-1}\) & 1241 cm\(^{-1}\) within ± 3 cm\(^{-1}\). For that particular sample (treated at 30 W and 2 min??? mention so.) these peaks are shifted to 1720, 1154 cm\(^{-1}\) and 1241 peak is absent. This suggests that for other samples the C=O and C-O environment has remained more or less static even after the plasma treatment although their intensities varied considerably suggesting cross linking [26]. In the present case in PMMA C=C does not exist and C=O & C-O are responsible for cross linking of the samples.

M. Matsuguchi et al [26] have shown that with the increase in the photo irradiation time there was a rapid decrease in the absorbance at 1630 cm\(^{-1}\) of the C=C stretching vibration. They have attributed this fall in intensity of the C=C absorbance peak to the degree of cross linking due to photo irradiation. They have concluded that with photo irradiation time the degree of cross linking goes on increasing until it reaches a maximum after which it remains constant. The peaks at 1149 and 1241 are clearly observed, Ulrike et al [27] also observed those peaks at 1150 cm\(^{-1}\) and 1240 cm\(^{-1}\) separately and
with sufficient intensity. The %transmission peak intensity of C=O and C-O showed an overall decrease with increased power.

Choi et al [28] have studied chemical changes in PMMA caused by various irradiations like UV, X-ray, electron and proton beams. They have suggested that gaseous products like CO, CO$_2$, CH$_4$ and main chain scissions may have caused due to irradiation leading to formation of new bonds in the polymer chain, cross linking being one of them. They have further confirmed that the decrease in the carbonyl bond intensity is proportional to the incident dose of different radiations used.

The changes are also observed in the PMMA films exposed to plasma in the present work. The argument by Choi et al [28] that chain scission and the formation of new bonds due to irradiation by UV, X-ray, electron and proton beams can also be extended in case of the present work. This is because there are various species available in the plasma for interaction with matter, but the exact estimate of them is difficult.

The C=O and C-O absorption peaks (write peak values) in all the argon plasma treated samples (for power variation at constant time of 2/5/8 min) were narrow and distinct only their % absorption intensity changed. These results can therefore be compared with those of Ulrike et al [27]. The % absorption peak intensity of C=O and C-O showed an overall decrease with increased power at constant time.

In case of samples treated for 5 and 8 min at 20, 30 and 40 W it is interesting to note that there is an increase in C=O as well as C-O functionality. The increase in C-O can be due to formation of new C-O functionality as we had also observed loss of C-C 1640 cm$^{-1}$ in the FTIR spectra. This could be attributed to the fact that at this power, time and pressure the oxygen present in the reactor (the reactor pressure was 0.2 mbar) could have got incorporated into the material. This is in good agreement with the work carried out by Vargo Gradilla [29]. They have studied the surface modification of PMMA by O$_2$/H$_2$O and H$_2$O RF glow discharge plasmas. They had observed an increase in the carbonyl functionality in PMMA after O$_2$/H$_2$O RF plasma treatment for 10 min.

3.2.3.2 The SEM of the Plasma Treated Samples:

To observe the surface roughness or the extent of micro-pore or cracks formation, the SEM was taken of all selected samples namely argon plasma treated with 20Watt power applied for 2,5,& 8 minutes, 30 Watt power applied for 2,5,&8 minutes, 40Watt power applied for 2,5,&8 minutes.
Micrographs are shown in Fig- 3.12. Micro pores were observed all over the sample surface at a low magnification X1000 and at higher magnification of X5000 these pores are found to be 1 to 3 μm wide. The micrographs shown for all the samples are taken at same magnification.

<table>
<thead>
<tr>
<th>2 Minutes</th>
<th>5 Minutes</th>
<th>8 Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>20Watt</td>
<td>30 Watt</td>
<td>40 Watt</td>
</tr>
</tbody>
</table>

Fig-3.12: SEM of plasma treated samples

The pore density was low (20W/2 min. sample) compared with the samples treated at higher powers and longer times. When observed under the SEM, the untreated samples showed a very smooth surface at all magnifications and also at high resolutions. In the present work, it has been observed from the FTIR and SEM that plasma treatments have lead to various modifications in the polymer like cross linking, changes in molecular weight and free volume due to scissioning, introduction of hydrophilic sites (C=O) and increase in porosity leading to surface roughness. One or more of the parameters may be responsible for giving the observed response of films to humidity.
3.2.4. Humidity Response of the Argon plasma Treated Films:

Humidity response of the plasma treated films is measured in terms of change in capacitance at 5000 Hz using LCR meter (Agilent 4284A). Change in capacitance with respect to humidity of three samples plasma treated with the power at 20, 30 and 40 Watt for 2, 5, and 8 minutes are given in Fig.15(a-d) and their outputs are compared with the output obtained for spin coated films with different spin speeds.

Fig-3.13.: Capacitance change w.r.t. humidity for plasma treated and spin coated samples

a) 20 W, b) 30 W, c) 40 W, d) Spin Coated films.

Fig. 3.13(a-c) represent change in capacitance with humidity of plasma treated samples at 20 watt, 30 watt, 40 watt respectively and Fig 3.13(d) is for spin coated samples with different speeds.
These graphs indicate that at 5000Hz frequency due to plasma treatment, output increases in the linear fashion as the humidity was increased. The reasons for change in output for films treated for different time intervals may be surface roughness - pore size and pore density. As these films are treated at the powers of 20-40 W, surface roughening is quite possible. This change occurs due to surface modification. While for the spin coated sample, its output response is slowly increasing up to the humidity of 53%. Afterwards it increases in the linear fashion. The reason behind this behavior is in the spin coated samples water did not get absorbed in the material, but it remains on the surface only. So the change in capacitance occur is small initially and as humidity increases the output increases after 53% humidity.

It is also observed that the maximum change in capacitance in whole range of humidity for plasma treated samples is 7pF and that for spin coated sample it is 3pF. The dielectric constant of PMMA is 2.6 and that of water is 80, the uptake of water into the polymer leads to changes in the overall dielectric constant of the material hence leading to change in the capacitance of the sensor with %RH. Further plasma treatments have lead to various modifications in the polymer like, cross linking, changes in molecular weight, free volume due to scissioning, introduction of hydrophilic sites (C=O) and increase in porosity leading to surface roughness. One or more of the parameters may be responsible for giving the observed response of films to humidity.

The nature of the RH response curves follow specific trend over the entire range of RH that was measured. Overall it is noted that the slopes (pF/%RH) of the curves are different for different treatment time and different powers. Those values are tabulated below (Table 3.3).

<table>
<thead>
<tr>
<th>Power.</th>
<th>Treatment time</th>
<th>20W</th>
<th>30W</th>
<th>40W</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 Minutes</td>
<td>0.0375</td>
<td>0.03888</td>
<td>0.0355</td>
</tr>
<tr>
<td></td>
<td>5 Minutes</td>
<td>0.07125</td>
<td>0.07825</td>
<td>0.04375</td>
</tr>
<tr>
<td></td>
<td>8 Minutes</td>
<td>0.03525</td>
<td>0.03375</td>
<td>0.02713</td>
</tr>
</tbody>
</table>

The sensitivity values obtained are low, probably due to the small thickness (2-6μm) of the films. Again water in that situation may not get into whole of the thickness of the material irrespective of microporosity of the surface. So change in capacitance occurred is small w.r.t. change in humidity.
Surface roughness is another factor which is responsible for sensitivity changes. If SEM shown in the fig (3.12) are observed, it is noted that as time of treatment is increased, number of pores are increasing. It means that the samples treated for 8 minutes should show maximum sensitivity factor, but that is not observed. On the contrary for 8 minutes the sensitivity factors are less than other samples. This may be due to the pore size variations. The pore density is increasing but the pore size is decreasing with the increase in treatment time as well as with treatment power.

Therefore one can say that both surface roughness and hydrophilicity may in addition to some other factors contribute to the overall sensitivity of the sensor.

Other factors which have to be considered are cross linking and change in molecular weight and free volume of the polymer due to plasma treatment. Cross linking is evident in most samples but their degree is difficult to calculate as derived from FTIR analysis. The change in the molecular weight is difficult to predict. It has been proposed that increase in the molecular weight leads to increase in the water uptake whereas decrease in the molecular weight leads to closer molecular packing leading to decrease in the available free volume necessary for water uptake[30]

According to Andrew et al [30] the differences in the free volume in the polymer is mainly responsible for the observed differences in the sensitivity of the sensors. The dual–state model of gas sorption has been widely used in the interpretation of gas diffusion in amorphous polymers including PMMA. In this model, sorbed gas molecules are interpreted as being a part of one of two populations in the polymer, the Henrian population of molecules sorbed by ordinary dissolution mechanisms in the polymer, and the Langmuir population residing in the free volume within the polymer.

The concentration of water sorbed in the Henrian sites in these films will depend on the availability of hydrophilic sites like C=O in case of argon treated samples. The Langmuir population (dependent on the free volume available in the polymer) of the sorbed gas molecules on the other hand will depend on the available free volume which in turn will depend on the cross linking density and degree of packing porosity, and the presence and absence of side groups of the polymer backbone. Other factors which contribute to the water uptake are molecular weight and surface roughness.

Turner D.T. [30] has studied the sorption kinetics and volumetric changes in PMMA sheets, where by after the immersion of PMMA sheets in water for a week he observed that the total percentage increase in weight of the samples leveled off near 1.2% in which about one-half of the water was observed to be accommodated in micro voids. Further, Turner D.T. [31] studies on effect of molecular
weight suggest that samples of low molecular weight \((M_w = 60600, M_n = 33200)\) take up only 1.2 % water as compared with the samples of high molecular weight \((M_w > 10^6)\) which take up water up to 2.0%. From the density changes which accompany water sorption it is estimated that a low molecular weight sample accommodated only 15% water in micro voids whereas about 50% of water was found in samples of high molecular weight. This suggests that lower molecular weight means closer molecular packing leading to lesser micro void formation.

If we once again observe the \(C=O\) intensity in these samples it is observed that the \(C=O\) absorption peak increases as we increase time of treatment. Once again it is to be noted here that these samples with well defined \(C=O\) absorption peaks did not give any improvements in the sensitivity, on the contrary these samples showed lesser sensitivity (treatment time of 8 min.) than the untreated sample suggesting the bulk properties of the polymer may have changed due to plasma treatment leading to changes in the free volume.

All the factors discussed above are responsible and play a crucial role in determining the uptake of water in the polymer. The percentage contribution of each factor in the water uptake is however not known but the availability of free volume and the presence of hydrophilic sites are major contributors in the water uptake mechanism.

As the degree of cross linking, scissioning (availability of free volume), changes in molecular weight, hydrophilic sites available, and porosity is different in all the samples due to various plasma parameters, the sensitivity shows wide variations. The sensitivity is also not uniform throughout the RH range being measured; this is due to the fact that the percentage of all these factors responsible for water uptake at various depths in the polymer could be different for different samples which in turn are plasma parameter dependent.

**Response time of plasma treated films:**

The time interval in min between 90% and 10% of the maximum capacitance (at saturation) value is defined as response time and is calculated from Capacitance Vs time graph. Fig 3.14 shows the response curves of the plasma treated films treated at 30 Watt for 5 min since this film gave maximum sensitivity.
Fig-3.14: Response and recovery time of film.

The response time for sample plasma treated at 30watt for 5 minutes is 6 min and recovery time of same sample was 7 minutes which is better than 7 to 14 min. reported by Dabhade et.al.[10]. Kulwiki [11] has suggested that typical equilibration time for polymer based sensors to be around 15 min which he has further set as programmed time for sensor characterization measurement. The observed time in the present work 6 min and 7 minute is of similar order suggested by Kulwiki [11].

3.2.5 Hysteresis:

Hysteresis defined as the maximum difference in the two outputs (increasing and decreasing cycle) at the same RH level. It is observed to be nearly 4% for plasma treated sample at 30 watt. The hysteresis in the response at lower RH is a result of slow desorption of water from the surface of PMMA. At higher humidity, the condensation occurs and forms a cluster over the surface of the film, which attributes to hysteresis. Here, hysteresis for plasma treated sample at 30 watt for 5 minutes film is shown in fig.3.15. For other films also hysteresis of the order of 4 to 7% was observed.
Fig-3.15: Hysteresis result for 30W/5 min. film

During increase in the %RH the response increase in RH is slow and the change in capacitance is not much as the humidity is also low. After 50%RH the sensor starts to show the variation in capacitance gradually up to about 75%RH when the sensor response is fast. The sensors do not show the initial capacitance as the sensors were removed from the RH chamber after the maximum RH was reached and as they require more to equilibrate the initial capacitance can only be retained after the sensor is kept at maximum RH for more than 15 min. Due to this cycle the sensor shows a large hysteresis in the static mode of RH sensing.

Hysteresis is related to film thickness, since measurements are performed using fixed time intervals and thin films equilibrate faster than thicker films. Other contributions to differences in capacitance include process variations which lead to differences in dielectric permittivity of the material and contact problem.

Another reason for large variation in hysteresis from sample to sample can also be attributed to the fact that the samples have a considerable response time therefore during the dynamic response the sensor does not immediately respond to the changes in humidity which leads to hysteresis. According to Andrew *et al* [23] hysteresis in polymer films is caused in part by the mechanical relaxation of the polymer when the water is sorbed. Relaxation to the low-RH state is not instantaneous, so removal of water lowers the cohesive energy density of the polymer, requiring a larger difference in chemical potential between water in the ambient and water in the polymer to remove the water. Addition of cross-links to the polymer will increase the dimensional stability by limiting the movement of polymer chains in any relaxation that occurs. Thus hysteresis is expected to be lower in the cross-linked PMMA.
3.3: Plasma Polymerized PMMA as humidity sensor- Results and Discussion

3.3.1: Introduction

This section describes the results on monomer purification, deposition of plasma polymerized MMA (PPMMA) films at various system parameters and characterization of the deposited films by SEM, FTIR and RH sensing. The results are discussed in view of the available literature.

3.3.2: IR Analysis of the Purified Monomer:

In the commercially available monomer (MMA) very small percentage of quinone (150 ppm) is added as inhibitor to prevent polymerization. The monomer was distilled using the procedure described in section 2.3.3. The IR spectra of undistilled and distilled MMA are shown in Fig. 3.16 (i) and (ii). Change observed in the spectrum indicates that the monomer is properly distilled. All the peaks observed in conventional PMMA (see section 3.1.3) are observed in distilled monomer. Standard IR spectrum is taken from Aldrich Library [32] and compared with the results obtained. It confirms the purification of the monomer. Further no peak is observed at 3450 cm\(^{-1}\) which corresponds to OH stretching, indicating the absence of moisture in the monomer.

![Fig-3.16: IR spectra of MMA (i) Un distilled (ii) Distilled (iii) Standard Aldrich](image-url)
This purified monomer is then used as a starting material for the plasma polymerization of the methyl methacrylate [10].

3.3.3 Synthesis of Plasma Polymer Films

It is observed from the literature [33] that the main variable parameters for plasma polymerization are the monomer flow rate, carrier gas flow rate, system pressure, input RF power and reactor dimensions. Hattori et al [34] carried out plasma polymerization of MMA in an inductively coupled, tubular type reactor at system pressure of 1 Torr, argon flow rate of 40 cc/min., MMA flow rate of 3 cc/min and the input power of 20 W. Gangal et al [35] had carried out depositions of PPMMA in a reactor similar to the one used by Hattori where they varied the pressure from 0.2 Torr to about 1 Torr. The typical argon flow rate was 50 cc/min and the monomer flow rate was varied between 10-50 cc/min. The input power used was from 30 to 60 W.

Using above parameters as guidelines, depositions in the present work were carried out in a similar inductively coupled tubular type reactor [33,34]. A large number of experiments were carried out in order to get deposition of plasma polymerized films having same chemical structure. Many experiments with various combinations of power, pressure and flow rates were carried out to deposit the films, for RH sensing.

The typical conditions used were in the ranges, argon flow rate between 5-15 cc/min, MMA flow rate 20-30 cc/min; pressure 0.1-0.4 mbar and the RF power 10-45 W. The time of deposition was kept constant at 1 hour to get sufficiently thick films. Plasma polymerized films were formed only at certain combinations in the above given ranges of parameters.

The oily films were obtained at relatively high pressure (0.4 mbar). The RF power used during these depositions was also considerably higher i.e. 60 W. Such high power was necessary to obtain the glow in the polymerization region at high pressure. At lower discharge power and pressure of 0.4 mbar, the glow does not extend to the substrate holder, which is necessary for the polymer deposition on to the substrate. These were not used for further characterization.

Formations of oily films indicate that oligomers are formed at high system pressure and high RF power. This observation is similar to the one reported by Duval and Theoret [36], they suggest that at
high reaction pressure, (> 1 Torr) there is sufficient monomer on the surface of the substrate to dissolve the reaction chain and limit the degree of polymerization. This leads to the formation of low molecular weight oily products. This observation implies that fragmentation of the monomer may be taking place.

Liepins and Sakaoku [37] carried out plasma polymerization experiments in an inductively coupled plasma in the pressure range between 0.6 to 3 Torr. They have reported that polymeric powders are formed nearly exclusively in an inductively coupled RF reactor where organic vapor is introduced in the plasma of carrier gas. They have further reported that powdery film formation at higher pressures also depends upon the structure of the monomer used. Methyl methacrylate however lies in the list of monomers which do not form powdery films[37]. Formation of oily films and not powdery films at higher pressures in all our experiments is supported by this result. Duval and Theoret [36] found that high molecular weight is favored by low pressure and high power. They concluded that at low pressure the surfaces are monomer deficient and the reactive species continue to grow yielding high molecular weight solid products. These observations were later verified by Kobayashi et al [38].

Films formed at pressure 0.2 mbar, argon flow rate (5cc/min), MMA flow rate (25 cc/min) and time of deposition (1 h ) are the fixed parameters with different RF power from 10 to 45watt were subjected for further investigations. All the films were reproducible when similar parameters given above were maintained.

3.3.4: Characterization of the plasma polymerized films:

3.3.4.1 FTIR:

Three samples (one silicon and two IDT substrates) were deposited at each power level in the range 10 to 45W. Samples deposited on silicon are used for FTIR measurement and remaining two samples were used for humidity measurement. Thickness was measured using talystep method (Taylor Hobson, Fukuoka, Japan). It was found to vary from 150 to 250nm in the power range used. The films deposited on the silicon substrates showed color striations on the surface, which is created because of the variations on the thickness deposited on the substrate. FTIR spectra of the films deposited under various power conditions are taken. The FTIR spectrum of conventional PMMA is used for comparison. All the absorption peaks of PMMA are also observed in the PPMMA.

The representative IR spectrum of the films is shown in Fig-3.17.
Fig-3.17: FTIR spectra of PPMMA samples

Table-3.4 IR absorption peaks for films at different RF power (10 to 45W)

<table>
<thead>
<tr>
<th>Wave number conventional PMMA cm(^{-1})</th>
<th>Peak assignments</th>
<th>Absorption peaks obtained for PPMMA films deposited at different power levels cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 Watt</td>
</tr>
<tr>
<td>3450 O-H stretch</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>2950 CH(_2) stretch</td>
<td></td>
<td>2958</td>
</tr>
<tr>
<td>1730 carbonyl group</td>
<td></td>
<td>1715</td>
</tr>
<tr>
<td>1640 C=C stretch</td>
<td></td>
<td>1634</td>
</tr>
<tr>
<td>1430 CH bend in CH(_2) group</td>
<td></td>
<td>1435</td>
</tr>
<tr>
<td>1370 CH bend in CH(_3) groups</td>
<td></td>
<td>1370</td>
</tr>
<tr>
<td>1140 C-O stretch</td>
<td></td>
<td>1111.5</td>
</tr>
</tbody>
</table>

The peak positions are shown in Table 3.4. Column 1 of Table 3 gives the FTIR absorption peaks of conventional PMMA. Column 2 gives the corresponding assignments. Remaining 8 columns give the absorption peaks obtained of the films deposited under different power conditions. As can be seen from the table the peaks observed in PPMMA films are near to the ones in conventional PMMA but are different in films deposited under different power conditions.
As shown in the table, for 10W to 30W all the peaks are very close to the standard peak values of PMMA except the peak at 3450 cm\(^{-1}\). As this peak is not present, it indicates absence of moisture in monomer at the time of distillation and so complete loss of the O-H stretch at 3450 cm\(^{-1}\).

The IR spectrum shows absorption peaks at wave numbers 3450 cm\(^{-1}\) due to OH stretch, 2950 cm\(^{-1}\) due to CH\(_2\) stretch, 1730 cm\(^{-1}\) due to carbonyl group, 1430 cm\(^{-1}\) for CH bend in CH\(_2\) group, 1370 cm\(^{-1}\) for CH bend in CH\(_3\) groups and 1140 cm\(^{-1}\) due to ester group. These peaks are all at similar wave numbers compared to conventional PMMA (refer to Table-(3.3.1). The only difference is that the absorption peaks are broader than the conventional PMMA and seem to be merged indicating the formation of cross linked polymer [23] The IR analysis thus confirms the formation of the polymer.

These results are well in agreement with the results of Tobin et al [39], wherein they have found that the index of refraction ‘n’ of PPMMA films is inversely proportional to the deposition pressure at constant plasma power. The density is presumed to increase with the increasing ‘n’. They have inferred that films produced at higher pressures can be termed as ‘low-density’ and those deposited at lower pressures as ‘high-density’ films.

In the present case the films deposited at lower pressure of 0.2 mbar could also be of high density in nature as they showed broadening and merger of absorption peaks in the FITR spectra suggesting cross linking. Therefore we can further say that more cross linking may lead to higher density of the PPMMA.

It is reported by Suzuki et al [40], that the humidity sensor that contains well designed carbonyl group as adsorption sites will respond directly to RH. As is evident from the FTIR spectra, all the films deposited in the present work contain well defined carbonyl group at 1730 cm\(^{-1}\) and therefore are supposed to be sensitive to humidity. The intensity of the carbonyl peak is however varying depending on the polymerization conditions and degree of cross linking. For 35 and 45W films, the peaks obtained are very much close to the standard PMMA peak value.

From 25W to 45W, all the peaks are absent at 1640 cm\(^{-1}\) of the C=C stretching vibration, probably due to high wattage.

The absorption peaks of 15, 40 and 45W especially in the range 1000-1200 cm\(^{-1}\) are seen to be broader indicating the presence of cross links. The band due to ester C-O stretching mode at 1140 cm\(^{-1}\) is broad in 15, 40 and 45W samples which confirms characteristic of cross linked polymer. In the present work the decrease in the absorption peak followed by broadening for some samples is more attributed to cross linking and the extent of cross linking is different for different samples [10].
Summing up the work on variation in power at fixed time, one can say that in the present work the decrease in the absorption peak followed by broadening for samples 15W, 40W, and 45W is more attributed to cross linking. Out of these eight samples, from FTIR table it is observed that most of the peaks for 35W sample are close to standard peaks. But we are not getting peak near 1640 cm\(^{-1}\). The reason is to be analyzed.

3.3.5: **Humidity Response of the plasma polymerized Films:**

Humidity response of the plasma polymerized films is measured in terms of change in capacitance at 5000 Hz using LCR meter (Agilent 4284A). Fig.3.3.3 shows the change in capacitance with respect to humidity of all samples formed from 10 watt to 45 watt power.

![Humidity Response Graph](image)

**Fig- 3.18: Capacitance change w.r.t. humidity for plasma polymerized samples.**

As seen from fig-3.18, the variation of capacitance is different in different humidity regions for a particular film and these humidity ranges vary from film to film. Broadly speaking there are two regions, in lower humidity region( around 12-53% ) the sensitivity is low and at higher humidity region (above around 53%) the sensitivity increases suddenly. The reason of this increase probably lies in the structure of the films and the readings are taken at the room temperature and room environment. However the detailed investigation are yet to be done. Table 3.5 gives the values of sensitivities in two different humidity ranges for different films.
Table 3.5 Sensitivity of PPMMA films.

<table>
<thead>
<tr>
<th>Plasma power</th>
<th>Low humidity region</th>
<th>High humidity region</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.016</td>
<td>0.335</td>
</tr>
<tr>
<td>15</td>
<td>0.024</td>
<td>0.235</td>
</tr>
<tr>
<td>20</td>
<td>0.015</td>
<td>0.181</td>
</tr>
<tr>
<td>25</td>
<td>0.045</td>
<td>0.27</td>
</tr>
<tr>
<td>30</td>
<td>0.035</td>
<td>0.362</td>
</tr>
<tr>
<td>35</td>
<td>0.017</td>
<td>0.196</td>
</tr>
<tr>
<td>40</td>
<td>0.013</td>
<td>0.167</td>
</tr>
<tr>
<td>45</td>
<td>0.013</td>
<td>0.204</td>
</tr>
</tbody>
</table>

Higher sensitivity of the PPMMA films is interpreted as a larger concentration of sorbed water caused by a higher free volume in the PPMMA film. In the present case the cross linked polymer can be regarded as a high molecular weight material accommodating more water in the network structure.

The variation of sensitivity from film to film is attributed to the difference in the free volume in the sensor films, presence and intensity of the carbonyl group and the molecular topology of the films [23].

While explaining the results obtained on PPMMA films deposited in parallel plate plasma system Andrew et al [23] have used a dual-state model of gas sorption. In this model, sorbed gas molecules are interpreted as being part of one of two populations in the polymer, a Henrian population of molecules sorbed by ordinary dissolution mechanisms in the polymer and Langmuir population residing in the free volume within the polymer. Because the PPMMA and PMMA films can be regarded as basically identical as PPMMA and PMMA have been formed from the same basic monomer-MMA, the concentration of water sorbed in the Henrian sites can be viewed as being the same in these films.

The difference in the sensitivity of PPMMA films compared to PMMA films is regarded to be due to the adsorbed water in the Langmuir population. Higher sensitivity of the PPMMA films relative to the PMMA films is interpreted as a larger concentration of sorbed water caused by a higher free volume in the PPMMA film. The PPMMA films thus have low density, though they are cross-linked, which varies as the deposition conditions. The films deposited under different deposition conditions have shown
different sensitivity to RH. The differences in the dielectric behavior of the PMMA and PPMMA films reveal details of the difference in structures between the two materials.

Andrew et al [23] have reported the sensitivity of PPMMA films to relative humidity. The films were deposited in parallel plate reactor. However, their work show sensitivity lower than PMMA which is reported to be due to the high density of cross linking implying less free volume within which water will be adsorbed in Langmuir population.

Turner D. T. [31] has reported that samples of PMMA of low molecular weight may take up less water than samples of normally high molecular weight. Turner has also concluded that, from the density changes accompanying water sorption it is estimated that a low molecular weight sample accommodated only 15% water in microvoids, as compared with 50% for samples of high molecular weight. In the present case the cross linked polymer can be regarded as a high molecular weight material accommodating more water in the network structure. In linear glassy polymers closer molecular packing may be the cause of the material accommodating lesser amount of water.

The difference in the obtained density of cross-linking in the present work as compared to the reported work by Andrew et al [23] may also be attributed to the difference in the reactor used. In the present study we have used an inductively coupled reactor.

3.3.6 Response and recovery Time of plasma polymerized films film:

To determine the response and recovery time of the sensor, the graph of change in resistance Vs time is plotted. (Fig. 3.19) From this graph the response and recovery time is calculated. Response time of the film is 118 sec and recovery time is 63 sec which is slower than reported value of 30sec [23]. The reason of this increase probably lies in the structure of the films. Here we tried all the films but we got good result for 35W film.

![Graph](image)

Fig-3.19: Variation of Resistance with time for 75% humidity
3.3.7 Hysteresis of plasma polymerized films:

Hysteresis defined as the maximum difference in the two outputs (increasing and decreasing cycle) at the same RH level. It is observed to be nearly 2% for plasma polymerized samples at 35 watt. The hysteresis in the response at lower RH is a result of slow desorption of the water from the surface of PMMA. At higher humidity, the condensation occurs and forms a cluster over the surface of the film, which attributes to hysteresis. Here, hysteresis for plasma polymerized sample at 35 watt film is shown in fig-3.20. For other films also hysteresis of the order of 2 to 5% was observed. Representative graph of only one sample is given.

![Graph showing absorption and desorption](image)

Fig-3.20: Hysteresis result for 30W film

3.4 Conclusion:

Comparative study of spin coated, plasma treated and plasma polymerization films as humidity sensor

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Spin Coated Film</th>
<th>Plasma Treated Film</th>
<th>Plasma Polymerized Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response time</td>
<td>10 minutes</td>
<td>6 minutes</td>
<td>118 sec</td>
</tr>
<tr>
<td>Recovery Time</td>
<td>12 minutes</td>
<td>7 minutes</td>
<td>63 sec</td>
</tr>
<tr>
<td>Hysteresis</td>
<td>1%</td>
<td>4%</td>
<td>2%</td>
</tr>
<tr>
<td>Repeatability</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>Good</td>
<td>Good</td>
<td>Not good</td>
</tr>
<tr>
<td>Ease of Construction</td>
<td>Very easy</td>
<td>Easy</td>
<td>Depends on system</td>
</tr>
</tbody>
</table>
From above table, it is observed that plasma polymerization system can be preferred as the sensor formed by that system has the minimum response and recovery time. But on the other side to form a film of 2000 Angstrom thickness, the system requires minimum one hour. Also depending upon the type of system, its reproducibility also changes. So it is better to use a method by virtue of which good sensor can be built in minimum time interval. So spin coating is preferred. Its response time is large but by using some surface modification method it is possible to modify its surface to get quick response of the film. One of the methods is plasma treatment.

References:
10. B. Schneider; J. Stokr; P. Schmidt; M. Mihailov; S. Dirlikov; and N. Peeva; Polym. 20 705(1979).
32. C. J. Poucher; The Aldrich Library of IR Spectra; Aldrich Chemicals Company Inc., Milwaukee, US.
34. S. Hattori; J. Tamano; m. yamada; M. Ieda; S. Morita; K. Yoneda and S. Ishibashi; *Thin Solid Films* 83 (1981) 189.
40. K. Suzuki; Y. Nabeta; and T. Inuzuka; Tech Digest, 10th Sensor Symp Tokyo, Japan; pp 61-64(1991).