Chapter I

Theoretical background and Literature Survey

1.0 Introduction

Humidity sensors have gained increasing applications in industrial processing and environmental control [1, 2, and 3]. For manufacturing highly sophisticated integrated circuits in semiconductor industry, humidity or moisture levels are constantly monitored. There are many domestic applications, such as intelligent control of the living environment in buildings, cooking control for microwave ovens, intelligent control of laundry etc. In automobile industry, humidity sensors are used in rear window defoggers and motor assembly lines. In medical field, humidity sensors are used in respiratory equipment, sterilizers, incubators, pharmaceutical processing, and biological products. In agriculture, humidity sensors are used for green-house air-conditioning, plantation protection (dew prevention), soil moisture monitoring, and cereal storage. In general industry, humidity sensors are used for humidity control in chemical gas purification, dryers, ovens, film desiccation, paper and textile production, and food processing. Other fields of interest are meteorological services, civil engineering and many more. In all these applications there is a strong need for reliable, accurate and low-cost humidity sensors, especially for low relative humidity (RH) conditions.

There are many methods/principles used to measure humidity [4, 5, 6], ranging from mechanical devices, wet-and-dry bulb hygrometry, chemical color change systems, optical fibre systems, dew point hygrometry, infrared absorption and LiCl cell, resonant frequency, thermal conductivity, surface acoustic wave (SAW) and electrical impedance change. As far as electrical impedance change sensors are concerned, which is the topic of this thesis, there are two types of - capacitive type and resistive type.

Resistive-type sensors rely on a change of the electrical resistance of a hygroscopic medium such as a polymer film, sintered ceramic film, salt or treated substrate. Resistive-type sensors exhibit a logarithmic response to humidity (typically 1 kΩ — 10 MΩ between 90 and 10%RH) and require sophisticated electronics to interpret. In addition, resistive-type sensors do not respond well below 20%RH. However, they offer good interchangeability and are generally cheaper to manufacture than capacitive-type sensors.

Capacitive-type humidity sensors rely on a change in permittivity (ε) of a ceramic or polymer dielectric with relative humidity. Capacitive-type sensors can be used in aggressive
environments such as the chlorinated air in swimming pools or ammonia present in livestock facilities. Capacitive-type sensors are more expensive to manufacture than resistive type sensors. It is also known that output of a capacitive-type humidity sensor gradually increases with long-term use in a hot and humid atmosphere. However, capacitive type sensors have several key advantages over resistive-type sensors: they exhibit a linear response to humidity, require less complex electronics to interpret and can operate over a wider RH range. The measurement of capacitance is the preferred method, since this property is less influenced by other gases and vapors.

The constructive design of a good humidity sensor is a rather complicated topic because high performance humidity sensors claim many requirements, including linear response, high sensitivity, fast response time, chemical and physical stability, wide operating humidity range, low cost, low hysteresis, and good resistance to chemical agents [5, 7].

A wide variety of ceramic, polymeric and composite sensors are being produced to serve the applications of humidity sensing. Each of these types of sensors however, has limitations, and new sensor concepts continue to emerge. Ceramic sensors [8] are based on adsorption of water molecules in the pores and grain boundaries of porous semiconducting materials such as certain modified spinels or alumina. The internal surface conduction increases with humidity. However, the internal surfaces can become semi permanently changed during prolonged exposure to humid atmosphere or contaminants such as oil vapor or smoke. An internal heater is required to periodically regenerate ceramic sensor and recover the humidity-sensitive properties that characterize the virgin sensor. This adds to complexity and cost. Devices without heaters are useful in low humidity applications or reasonably clean environments and some may require recalibration.

Polymer based humidity sensors present many advantages such as low cost, flexibility and easy processability [5,7]. The resistive-type sensors are fabricated with polymer electrolytes or polymer–salt complexes, while the capacitive-type with hydrophobic polymers. Some polymer–salt complexes have been reported to work as humidity sensors. Typical examples are poly (propargyl alcohol) doped with sulfuric acid, poly (pdiethynylbenzene- co-propargyl alcohol) doped with iron trichloride and poly(2-acrylamido-2-methylpropane sulfonic acid) doped with alkali salts. It is also reported that the doping of nanometer-size BaTiO3 with
Na$_2$CO$_3$ and NaH$_2$PO$_4$ can reduce the hysteresis in the RH-dependent impedance characteristics.

In polymer film capacitive-type sensors, the sensing film is often thin (5–25 µm) and produced by casting or extrusion methods [4]. Polymers such as polyimide, cellulose acetate butyrate (CAB), polymethyl methacrylate (PMMA) and polyethylene terephthalate (PET) are some of the materials employed in capacitive-type RH sensors. Poly(methyl methacrylate) (PMMA) is a promising candidate for polymeric sensors due to its processability and mechanical stability. However, water sorption experiments of PMMA revealed that the hydrophilic property of the carbonyl groups contained was not enough for sorption of water molecules.

Different types of polymers play an important role in optical sensors categorized as inorganic and organic e.g. poly(vinyl chloride) (PVC), poly(tetrafluoro ethylene) (PTFE), nafion, nylon, agarose, sol-gels, etc [3]. Conducting polymers are also in use as humidity sensors. Polyaniline is unique among the known conducting polymers because its conductivity is controlled by the doping levels of oxidation and protons. Oxidation states of polyaniline, whose electrical properties are sensitive to water, provide a basis for potential applications in sensors for humidity control. The aqueous environment changes the conductivity due to two reasons:
1. Adsorbed water molecules dissociate at imine nitrogen centers.
2. Positive charge migrates through the polymer.

An earlier study of this problem indicated that one of origins of this drift phenomenon was an irreversible increase in volume of the sensing polymer, presumably caused by swelling of the polymer in a hot and humid atmosphere [6]. The result suggests that the prevention of swelling in the sensing polymer is important in the preparation of stable capacitive-type humidity sensors. Cross-linking the polymer and formation of a rigid film are supposed to be effective for preventing such swelling phenomenon.

Plasma-deposited films have attracted increasing interest as materials for passivation, adhesion promotion, barrier coatings, optical waveguides, and relative humidity (RH) sensing applications [9]. Plasma deposition of films provides several advantages over the commonly used technique of casting films from resins. Film properties can be varied by adjusting the ratio of feed gases. Also, monomer gases that do not contain reactive sites for polymerization can be polymerized by the production of active species in the plasma. Material properties can also be controlled by adjusting the plasma-processing parameters such as reactor power and pressure.
Both Thin and thick film technologies are used for fabrication of sensors. The benefits of using thick-film technology for a humidity sensor are its inherent advantages of ruggedness and cost, while thin-film sensors offer smaller size and increased sensitivity. Although there are numerous thin-film polymer-based humidity sensors described in the literature and several low-cost commercially available humidity sensors, there are not many reports on comparison of performance. Studies of water uptake in polyimide film using a surface acoustic wave (SAW) sensor have demonstrated the ability of the SAW sensor to detect small changes in water uptake in polyimide. Therefore, the SAW sensor provides an alternative sensor configuration and may also yield information that could be useful for the optimization of a humidity sensor designed for low RH.

Present thesis concentrates on the comparative study of Plasma treated, Plasma Polymerized and Spin Coated PMMA Thin Film Based Humidity Sensors and their performance comparison.

1.1 Basic definitions of humidity [10, 11]

Humidity is a measure of the amount of water vapor dissolved in air (excluding any liquid water or ice falling through the air). The amount of water vapor present in atmosphere varies with time and location. The level of moisture present in the atmospheric air is known as ‘Humidity’ and specified by number of quantities such as absolute humidity, relative humidity, specific humidity, etc. The definitions for all are given as follows-

1.1.1 Absolute humidity [10,11]

The quantity of water in a particular volume of air at constants temperature is known as absolute humidity. The most common units are grams per cubic meter.

More technically: the mass of water vapor \( m_w \) per cubic meter of air and \( V_a \) is termed as absolute humidity as given in equation 1

\[
AH = \frac{m_w}{V_a} \quad \text{.......... (1)}
\]

The absolute humidity changes with change in air pressure which leads to problems in calculations where temperatures can vary considerably. Hence, absolute humidity
is generally defined as mass of water vapor per unit mass of dry air, also known as the ‘mass mixing ratio’ which is much more rigorous for heat and mass balance calculations.

### 1.1.2 Specific humidity \([10,11]\)

Specific humidity (SH) is a ratio of mass of water vapor to mass of air (including water vapor and dry air) in a particular volume. Specific humidity (equation 2) is expressed as a ratio of kilogram of water vapor \((m_w)\) per kilogram of mixtures \((m_t = m_d + m_w)\)

\[
SH = \frac{m_w}{m_d + m_w} = \frac{m_w}{m_t} \quad \text{(2)}
\]

Where,
- \(m_d\) - mass of dry air (kg)
- \(m_w\) - mass of water vapor (kg)
- \(m_t\) - mixture of dry air and water vapor (kg)

### 1.1.3 Relative humidity \([10,11]\)

Relative humidity (RH) is the ratio of partial pressure of water vapor in a gaseous mixture of air and water vapor to saturated vapor pressure of water at a given temperature. Relative humidity is expressed as the percentage and is calculated by using equation 3:

\[
RH = \frac{E(T_1)}{E(T_2)} \times 100\% \quad \text{(3)}
\]

Where,
- \(E(T_1)\) - saturated vapor pressure at temperature \(T_1\)
- \(E(T_2)\) - saturated vapor pressure at temperature \(T_2\)
- RH - Relative humidity of the gas mixture

Relative humidity depends on two factors: the amount of moisture available and the temperature. A change in relative humidity takes place either by adding water vapor available through evaporation or by changing surrounding temperature while holding the water vapor constant.

### 1.2 Methods for creating humidity:

Humidity sensitive materials have to be subjected to a number of known relative humidity values over the range of 0-100% RH at the given temperature of measurement in order to measure their response and to calibrate them. Hygrometers are used in many fields hence it is
essential to calibrate them for standard humid atmosphere. There are some useful methods to produce relative humidity. Four main methods as described below are used for producing humid atmosphere with varying relative humidity values.

a) Use of saturated salts
b) Divided flow method
c) Two pressure method
d) Two temperature method

1.2.1 Use of saturated salts: [10,11]

Large number of salts such as NaCl, P₂O₅, (NH₄)₂SO₄, H₂SO₄, KOH, KCl, LiCl etc. are used for producing relative humidity. These salts are used to produce super saturated solutions by dissolving them in water. The produced mixture is kept in an air tight chamber due to which at different temperatures, for different salts, the equilibrium vapor pressure of water in the chamber varies resulting in different relative humidity values. An air tight chamber is beneficial as the system is very sensitive to the changes in temperature for this the chamber must be thermally isolated from its surrounding. Normally a vertical gradient of water vapor pressure will be present in such a system. Circulating fans are introduced outside the chamber to help to eliminate the pressure gradient and to reduce the time required for equilibrium conditions. The drawbacks of this system are the time required for equilibrium is very long (number of hours or days also) and presence of salts may lead to deterioration of the sensor due to corrosion. The most common example is H₂SO₄ which is avoided in relative humidity control process.

1.2.2 Divided flow method: [10,11]

As suggested by the name the division of flow is useful for measuring relative humidity. An air or nitrogen is used as a carrier gas. Dry and saturated air/N₂ at constant temperature is mixed in different proportions using proportioning values to obtain different values of relative humidity. If X is the volume fraction of gas passing through the saturator or the saturated air then relative humidity is calculated using equation 4,

\[ RH = X \times 100\% \quad \ldots \ldots (4) \]

The accuracy of the system depends on the accuracy of designing of the proportioning value or the flow meters or the flow controllers. Only fixed values of relative humidity are possible. The method is quite popular owing to the fastness in varying relative humidity.
1.2.3 Two pressure method: [10,11]

Weaver [12] was the first investigator to use the principle of two pressure method which depends on the assumptions that the water vapor pressure in gas mixture remains the specified fraction of the total pressure when the total pressure changes. For a real ‘air-water’ mixture a small correction is required at low humidity.

The relative humidity calculation is done by equation 5,

\[ \text{%RH} = \frac{E_1}{E_2} \times 100 = \frac{P_1}{P_2} \times 100 \ldots \ldots \ldots \ldots (5) \]

Where,

- \( P_1 \): low water vapor pressure
- \( P_2 \): high water vapor pressure
- \( E_1 \): saturated water vapor pressure at \( P_1 \)
- \( E_2 \): saturated water vapor pressure at \( P_2 \)

The relation between water vapor and saturated water vapor pressure is given by equation 6,

\[ \frac{E_1}{P_1} = \frac{E_2}{P_2} \ldots \ldots \ldots \ldots (6) \]

The advantage of the method is that the relative humidity can be changed faster than the other methods. For example in the two pressure generator, the time required to reach steady state conditions at 20°C is 30 minutes.

1.2.4 Two temperature method [13,14]

In the ‘Two Temperature method’ air is saturated with water vapor at lower temperature (\( T_1 \)) and then heated to required temperature (\( T_2 \)) so that by varying \( T_1 \), different humidity conditions can be obtained. The relative humidity can be calculated with the help of equation 3 (section 1.1.3)

Many researchers tried to improve this method. C.L. cutting [15] gives a simple system which can be used for calibration of small sensors. The time required for steady, stable conditions to be achieved in this type of system is of the order of one hour at room temperatures.

1.3 Principles of Humidity Measurements
Humidity can be measured using a variety of principles. The principles and the corresponding operating mechanism are given in Table-1.2. The selection of the measurement principle is dependent on the material chosen and the application concerned.

Table-1.1: Principles of Humidity measurements

<table>
<thead>
<tr>
<th>Principle</th>
<th>Operating mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitance</td>
<td>Dielectric constant of material varies with H2O absorbed</td>
</tr>
<tr>
<td>Coulometric</td>
<td>Electrolyte is formed by absorption (P2O5+H2O); dc potential dissociates H2O. Current level is proportional to the moisture content.</td>
</tr>
<tr>
<td>Dew point</td>
<td>Temperature corresponding to condensation-evaporation equilibrium at a cooled surface; varies with H2O.</td>
</tr>
<tr>
<td>Gravimetric</td>
<td>A volume of moist air is exposed to a drying agent, subsequently weighed.</td>
</tr>
<tr>
<td>Hygroscopic</td>
<td>Length of the fiber varies with H2O.</td>
</tr>
<tr>
<td>Infrared</td>
<td>Absorption at 1.5 to 1.93 μm; split beam to compare sample cell and reference.</td>
</tr>
<tr>
<td>Microwave</td>
<td>Attenuation of radiation with H2O.</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>Hygroscopic coating changes crystal frequency.</td>
</tr>
<tr>
<td>RF-Sensor</td>
<td>Radio-frequency current due to dielectric change is a function of H2O.</td>
</tr>
<tr>
<td>Resistance</td>
<td>Conductivity depends on H2O absorbed.</td>
</tr>
<tr>
<td>Saturated salt (LiCl)</td>
<td>Self-heating to temperature of condensation-evaporation equilibrium measures dew point.</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Self-heated thermistors in bridge circuit; current imbalance due to difference in heat dissipation between atmosphere and reference cells.</td>
</tr>
</tbody>
</table>

In the present work capacitive type of sensors will be studied. Polymethyl Methacrylate, a hydrophobic polymer is used as a humidity sensitive material.
1.4 Polymers and their Characteristics:
Because of their versatility, their unique properties and ease of processing and fabrication, polymeric materials have found applications as plastics, elastomers, fibers, protective coatings and adhesives. In parallel with these well-established applications, new needs have emerged from technologies, which are still growing, such as microelectronics, optoelectronics, biotechnology and sensor applications.

Progress in organic and polymer chemistry has made possible the synthetic modification of polymer structure and the improvement in polymer properties to fit the desired needs [16].

1.4.1 Overview of Structures of Polymers [17]:
Polymers are large molecules with many (poly) repeatable units (mers). Polymer is a macromolecule. When a polymer contains only small number of structural units it usually is called as an oligomer. Three different types of polymers are shown in Fig-(1.3).

![Fig-1.1: Types of Polymers](image)

A linear polymer is a polymer in which the units in each molecule are linked together in a chain-like structure. A branched polymer is a polymer composed of molecules having a branched structure. A cross linked polymer is a polymer composed of macromolecules containing a three-dimensional network structures and for this reason are insoluble. A cross linked product, which is swollen by solvent, is called as a Gel. Cross linked polymers contain several network defects such as unreacted functionality, or chain ends, closed loops, entanglements. These defects influence the elastic properties of the polymer networks.
The polymer shape is considered to have two aspects: The polymeric configuration, which is the polymer shape formed by primary bonding and polymeric conformation, which is the polymer shape due to rotation around primary valence bonds.

1.4.2 The Glass Transition Temperature [17]:

The specific volume of (in mm/g or m$^3$/kg) an amorphous polymer like PMMA changes linearly with increasing temperature (see Fig-1.2) up to the transition region where a change of the slope occurs (steeper gradient). At certain temperature the rate of change of volume increases and a discontinuity is formed in the specific volume curve. This is known as glass transition temperature ($T_g$) and is usually defined as the point at which the tangents of the two curves intersect.

Below $T_g$, chain segments are frozen in fixed positions in a disordered quasi lattice. Some molecular movements of chain segments take place in the form of vibrations about a fixed position.

Fig-1.2: The specific volume of polymers as a function of temperature in the transition range
With increasing temperature, the amplitude of segmental vibrations increases. In the transition state, chain segments have sufficient energy to overcome the secondary intermolecular bonding force. Chain segments or chain loops may perform rotational and transitional motions (see Fig-1.3) which are called as segmental motion or short range diffusional motion.

Chain flexibility and intermolecular packing distances (chain stiffness), bulkiness, flexibility of side chain, and polarity of the chain are major parameters influencing $T_g$. Chain flexibility is determined by the ease with which rotation occurs about primary valence bonds. A rotation involves an energy barrier that is of the same order as the molecular cohesive forces (1-5 kcal/mol). The decrease in chain flexibility increases the $T_g$ temperatures by increasing steric hindrance. Steric hindrance is dependent on the size, shape and constitution of the backbone group. Rigid and bulky side groups decrease the flexibility of the chain (steric hindrance is increased) and the value of the $T_g$ is reduced. Introducing flexible side groups results in an increase of intermolecular distances; consequently free volume predominates and the $T_g$ is lowered. Other factors influencing $T_g$ are: crystallinity, tacticity, molecular weight, branching and intermolecular bonds.
All polymers exhibit a glass transition at a particular temperature or range of temperatures. Typical glass transition temperatures of various polymers are given in Table-1.1. The value of $T_g$ depends on the experimental time scale and the method of measurement. The values of $T_g$ reported in the literature for any particular polymer however, may vary from 10 to 30 °C [17].

### Table-1.1: Glass Transition Temperatures ($T_g$) of some Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (ethylene)</td>
<td>-80</td>
</tr>
<tr>
<td>Poly (isopropene)</td>
<td>-73</td>
</tr>
<tr>
<td>Poly (caproamide)</td>
<td>50</td>
</tr>
<tr>
<td>Poly (vinyl chloride)</td>
<td>83</td>
</tr>
<tr>
<td>Poly (styrene)</td>
<td>100</td>
</tr>
<tr>
<td>Poly (methyl methacrylate) PMMA Atactic</td>
<td>104 - 108</td>
</tr>
<tr>
<td>Isotactic</td>
<td>42 - 45</td>
</tr>
<tr>
<td>Syndiotactic</td>
<td>105 – 120</td>
</tr>
</tbody>
</table>

### 1.4.3 Free Volume Theory of Glass Transition:

The free volume $V_f$ in a polymer is defined by:

$$V_f = V_T - V_o$$

where $V_T$ is the total volume of the polymer at temperature $T$ (in degree Kelvin), $V_o$ is the theoretical molar volume for the most dense packing of the liquid molecules at 0K. The total volume of the polymer $V_T$ is the sum of the free volume $V_f$ and of the occupied volume $V_o$:

$$V_T = V_f + V_o$$

The occupied volume $V_o$ includes not only the Vander Waals radii but also the fluctuation volume, which is associated with the thermal vibrational motion. Cross linking reduces free volume and increases $T_g$. 

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1.4.4 Relaxation Process in the region of $T_g$ [17]:

The relaxation process in polymers can be considered as the movement of molecular segments of polymer molecules. For amorphous polymers, in the temperature region on either side of the $T_g$, three well-defined molecular relaxation processes often labeled with Greek letters $\alpha$, $\beta$, and $\gamma$ [18] are commonly observed.

(i) $\alpha$-relaxation is a process above $T_g$, considered as the primary process and referred to as the glass-rubber transition process. This relaxation process results from large-scale conformational rearrangements of the polymer chain backbone, which occur by a mechanism of hindered rotation around the main chain bonds.

(ii) $\beta$-relaxation is the process below $T_g$, considered as the secondary process and referred to as the glass transition process. This relaxation process results from hindered rotations of side groups independent of the polymer chain backbone.

(iii) $\gamma$-relaxation is the process below $T_g$ associated with the disordered regions of the polymer.

The $\alpha$-relaxation is observed at the highest temperature for a given frequency or at the lowest frequency for a given temperature as is usually connected with the glass transition, e.g. with large-scale molecular motions in the main and side chain of the polymer. The secondary relaxation processes, usually connected with limited motions of polar groups in the side chain, are observed in the glassy region of the polymer [19].

1.5 The Plasma State [20]:

At very high temperatures partial molecular dissociation reactions, excitations, and ionization mechanisms are initiated through electron expulsion process. Matter having equal number of simultaneously generated and oppositely charged particles and a different number of unionized neutrals has been recognized as the fourth state of matter and such ionized gases were termed as plasmas. Plasma is therefore an ionized gas.

Plasma contains a mixture of particles with different electric charges and masses. At a first approximation, the plasma may be considered thermally as consisting of two systems: the first containing electrons and the second containing heavy species, i.e. neutral species, ions and neutral molecular fragments.

The mechanisms in the plasma are excitation and relaxation, ionization and recombination. To maintain the steady state of electron and ion densities, the recombination
processes must be compensated by ionization processes, so energy must be continuously supplied to the system to sustain the plasma state.

1.5.1 Glow Discharge Plasmas (Cold Plasmas) [20]:

On the basis of electron temperatures and electron density the plasmas are classified into various types. Fig-(1.4) gives the classification of plasmas. The plasmas are also classified from the relative temperature of electrons and ions. If the temperature of the electrons is more than that of ions it is known as hot plasma and if the electron temperature is less than that of ions it is known as cold plasma. In the present work concentration is made on the cold plasma. Cold plasmas are also known as glow discharge plasmas.

The glow discharges can be generated by applying DC or RF potential across parallel plates or by inductively coupling the RF power to the gas. These methods are described in this article.
1.5.2 DC Glow Discharges:

A DC glow discharge is created by applying a potential between two parallel plates in a gas. Three important regions are observed in the glow discharge in 50 cm tube filled with neon as shown in Fig-(1.5):

- **Negative glow** – region of bright glow is observed near the **cathode**. This is a zone of high concentration of positive ions formed by collision with energetic electrons emerging from Crook’s dark space. Molecules in excited states are also formed in the negative glow region (thereby giving rise to a bright glow by relaxation to lower states) as well as negative ions and free radicals.

- **Dark Space** – Adjacent to the cathode is the comparatively dark region called as the cathode dark space or the Crook’s dark space. This corresponds to the sheath formed in the cathode region. This is the zone where the acceleration of positive ions to the cathode, and acceleration of electrons away from it is observed. A similar sheath is also formed in front of the anode but it is too thin to be seen clearly.

- **Positive column** – it is the region of the discharge which most nearly resembles plasma i.e. a partially ionized gas consisting of equal numbers of positive and negative charges. It can be considered as a channel for carrying current from the negative glow to the anode.

Typical distance between anode and cathode used for the plasma processes like sputtering, plasma treatment is around 5–10 cm. In this case the distance the positive column has negligible length leaving only the negative glow and the dark spaces adjacent to each other.
Fig-1.5: The Neon Discharge tube
1.5.3 RF Plasmas:

When the RF field is applied to the capacitively coupled electrode, the electrode surface in contact with the plasma is alternatively polarized positive and negative. When negative it attracts ions, and when positive it repels them. At high operating frequencies, the massive ions cannot follow the temporal variations in the applied potential but the electrons can. Thus a cloud of electrons that constitute the electron component of the negative glow plasma can be pictured as moving back and forth at the applied frequency in a sea of relatively stationary ions on the powered electrode. At radio frequencies (5-30MHz) the electrons oscillating in the glow have sufficient energies to cause ionizing collisions, thus reducing the dependence of the discharge on the secondary electrons and lowering the breakdown voltage.

The RF voltages can be coupled through any kind of impedance it is possible to use reactors without internal electrodes. Two most common techniques for coupling RF power into a glass tube, often refereed to as a tubular or tunnel reactor is by capacitive coupling or inductive coupling.

Most RF apparatus operate at frequency of 13.56 MHz this frequency is normally used for generating plasma. This frequency lies in the 10 to 20 MHz range that has been allocated by the Federal Communications Commissions for industrial use.

1.6 Polymerization:

Before one tries to understand the plasma polymerization process the prior knowledge of different mechanisms of polymerization is essential. In this article the conventional polymerization mechanism is discussed initially and then later the plasma polymerization mechanism is discussed.

1.6.1 Conventional Polymerization [21]:

Conventionally, polymers are synthesized via two mechanisms namely stepwise or condensation polymerization and by chain or addition polymerization.

1.6.1.1 Step Growth Polymerization [21]:

This is also called as poly-condensation. Here the polymer is formed by stepwise repetition of the same reaction again and again. For this to occur, the monomers which are capable of undergoing stepwise reactions must possess some active functional groups. If the
monomer is represented by \( \text{M} \) and the growing molecule by \( \text{M}_i \) step-growth polymerization can be represented as:

\[
\begin{align*}
\text{M} + \text{M}_1 & \rightarrow \text{M}_2 + \text{H}_2\text{O} \\
\text{M}_2 + \text{M} & \rightarrow \text{M}_3 + \text{H}_2\text{O} \\
\text{M}_n + \text{M}_m & \rightarrow \text{M}_{n+m} + \text{H}_2\text{O}
\end{align*}
\]

1.6.1.2 Chain-Growth Polymerization [21]:

This method of polymerization is also known as the addition polymerization. This is extensively used in industry. In this method a long chain molecule is formed by a series of consecutive steps in seconds and the products are the final polymer.

Addition polymerization can be schematically shown as:

\[
\begin{align*}
\text{Initiation} : \text{A}* + \text{M} & \rightarrow \text{M}^* \\
\text{Propagation} : \text{M}^* + \text{M} & \rightarrow \text{M}_2^*; \text{M}_n^* + \text{M} & \rightarrow \text{M}_{n+1}^* \\
\text{Termination} : \text{M}_n^* & \rightarrow \text{P}_n
\end{align*}
\]

Where, \( \text{M} \) is the monomer, \( \text{M}^* \) is the reactive species, \( \text{P}_n \) is the dead polymer and \( \text{A}^* \) is the initiator.

1.6.2 Plasma Polymerization:

Glow discharge polymerization or plasma polymerization has been known for many years; for example, Linder and Davies [22] described the gases and solids formed by some hydrocarbon vapors in a glow discharge in the year 1931. Later, Brick and Knox [23] have described the major features and variables associated with this process. Other articles have been published describing the chemical, physical [24] and electrical [25] properties of glow-discharge polymers.

In a glow discharge polymerization, organic vapors are introduced into a chamber at a pressure of about 1-5 Torr containing two parallel electrodes. An A.C. voltage is applied across the electrodes so as to initiate, and then to sustain, a uniform glow discharge in the intervening space. High energy ions and electrons are produced in the glow and these bombard both the
electrode surfaces and the molecules in the gas phase. These interactions initiate complex chemical reactions which result in the formation of thin (up to about 5 \( \mu m \)) uniform and continuous coatings on the electrode surface [26].

Plasma polymerization is a specific type of plasma chemistry resulting in the deposition of organic film. It refers to the deposition of polymer films through plasma dissociation and excitation of an organic monomer gas and subsequent deposition and polymerization of the excited species on the surface of the substrate. The deposited films are called plasma polymers and are generally chemically and physically different from the conventional polymer. Hydrocarbons, fluorocarbons and compounds containing nitrogen and oxygen and silicon have been used as starting materials for plasma polymerization[27].

The plasma polymers are characterized by the following features[27]:

- The films have thickness between 500 \( \AA \) to 1 \( \mu m \)
- Such films are highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal surfaces.
- The films are highly cross linked and can be made pinhole-free[27].
- The plasma polymers have no discernable repeating unit as do conventional polymers.
- The properties of the plasma polymer are not determined by the monomer used but by the plasma parameters. A product cannot be defined as the plasma polymer of ethylene; because a variety of products can be obtained from ethylene plasma therefore we can say plasma polymers of ethylene are not polyethylene.
- The monomer used for plasma polymerization does not have to contain a functional group such as double bond for the plasma polymerization to take place[28].

Plasma polymerization is thus a very different process from the conventional polymerization. For this reason, both the generally accepted terms “monomer” for the feed gas and “polymer” to describe the resultant film are strictly not correct since there is no repetition of unique repeat unit along a polymer chain. The real usually very different monomers are the plasma fragments that generate the deposit through homogenous and heterogeneous processes. Plasma polymerization is strongly system dependent process and can be controlled using the various plasma and plasma process parameters available with the experimenter.
1.6.2.1 Plasma Polymerization Mechanism [29]:

It is difficult to define a mechanism of plasma polymerization because of the very large number of elementary processes which must be considered. In order to interpret the kinetics of the polymer deposition in terms of a very simple reaction scheme with only small number steps, the nature of the species which propagate chain growth and the processes involved in initiating polymerization needs to be determined.

The elementary reactions leading to plasma polymerization can be grouped into five generic types—initiation, adsorption, propagation, termination and reinitiation. While in conventional polymerization the termination step interrupts the process, in the case of plasma polymerization chain fragments can be reconverted into radicals by collision with electrons in the gas phase or by impact of energetic particles or photon absorption on the surface of the polymer film. Polymerization in the gas phase and on the surface of the polymer film can be summarized by the reaction proposed by Poll et al[29]. The diagrammatic representation of the process is shown in Fig-(1.6).

Path K-1: Monomer directly polymerized into the growing film: plasma induced polymerization. This is essentially a conventional molecular polymerization process triggered by reactive plasma species. This can take place only if the monomer has polymerizable functional groups.

Path K-2 and K-3: The intermediate reaction products can be ions, excited molecules and free radicals and the monomer need not have polymerizable groups to undergo polymerization.

Ionization of a molecule by collision with an accelerated electron is an essential process for creating and sustaining plasma of the monomer with or without non-polymerizable carrier gas. In case of inert gas, ionization can occur by the elimination of an electron from an electron orbital and requires energy ranging from 12 to 25 eV. Therefore, in the process of ionization of inert gases, electrons having energies lower than ionization potential or off-centered collisions do not contribute to the ionization. In the ionization of organic molecules, the ionization energy required is generally greater than 10 eV, which is far above the bond energies of primary bonds in organic compounds. Therefore, low energy electrons and/or off-center collisions that can not ionize the molecule, can easily break the bonds in the organic molecules or create the exited species (dissociation of molecules) which can trigger the chemical reactions. These side reactions associated with ionization are absent in the plasma of inert and diatomic gases.
1.6.2.2 Physical Plasma Process Parameters:

When a monomer is introduced into a glow discharge the rate of plasma polymer deposition and the chemical and physical nature of the plasma polymer is affected by various physical plasma parameters which are at the experimenter's disposal. These are

- \( f \)-Frequency of the exciting potential (Hz).
- \( W \)- Excitation power (W).
- \( F \)-Monomer flow rate (Vol. (STP)/unit time)
- \( P_g \)-Plasma pressure (Torr).
- Geometrical factors like volume \((cm^3)\)
- \( T \)-Temperature of the deposition site (K).
- \( n_e \)-electron density
- \( f(E) \)-electron energy distribution
- \( N \)-gas density
- \( \tau \)-residence time (seconds).
The use of composite plasma process parameters is an alternate approach used for controlling the properties of the plasma polymer. One of the most widely used parameter is the W/F, power to flow rate ratio. It is argued that the chemical and physical properties of the plasma polymer will remain constant if the W/F ratio is maintained constant assuming that the pressure, monomer flow and the excitation frequency also remain constant. This is because W and F affect the basic plasma parameters $n_e$ and $\tau$. $n_e$ increases linearly with W and $\tau$ is inversely proportional to F. W/F ratio provides only a qualitative understanding of the polymerization process.

1.7 Plasma Treatment of Polymer Surfaces:

It has been known that the interaction of radiation with polymers can lead to the formation of three dimensional network structure, which generally improves the overall physical and chemical properties of the original substrate. This physical and chemical change in the polymer and the mechanism of cross linking and chain scission under exposure to radiation energies has already been established [30-32]. Apart from radiation various other methods of surface modification of polymers have been suggested and used to alter the polymer surface without affecting its bulk properties. These various methods include chemical treatments, flame treatments, coronas, low pressure plasmas, IR, UV, X-ray and $\gamma$-ray irradiation, electron and ion beam bombardment, ozone exposure and others [33].

The cold plasma conditions offer a unique route for the polymer modifications as the energies of the active species in the cold plasma conditions are high enough to split the chemical bonds from the organic derivative and consequently, tailored polymeric structures can be created by controlling the plasma conditions. This processing route offers possibilities of achieving unique surface characteristics of polymers for specific applications while the bulk structure and other properties of the polymer are maintained [34].

The surface modification by cold plasma range from simple topographical changes to creation of new chemistries and coatings that are entirely different from the bulk polymer. The surface modification is achieved by: Surface activation, deposition and grafting. The plasma treatments are also environment friendly and economical compared to other forms of treatments.

The effects of plasma treatment on the polymers are [28]:

- Create more reactive surfaces
- Affect wetting properties
- Cross linking
• Change in molecular weight of the surface layers

The main advantages of this technique are [35]:

• It is a clean dry technique and takes only minute to achieve.

• Only the surface properties of the polymer like the permeability, bondability and wettability are profoundly changed while the overall bulk properties of the material for which it was originally chosen remain unchanged.

• The surface characteristics of the polymer is dependent on the plasma parameters i.e. system pressure, gas flow rate, input power, which are under the control of the experimenter.

The processes which take place on the surface of the polymer due to plasma treatment are shown in Fig-(1.7).

![Diagram of Plasma Treatment Processes](Fig-1.7: Surface Modification of Polymers by Plasma Treatment)
1.7.1 Plasma Modification of Polymers:

The modification of polymer surfaces by electrical discharges excited in a variety of gases is a technique widely used as a method to increase the surface free energy or wettability of the material. The major virtues of the technique are: (i) it is a clean reaction and does not take much time and (ii) while making profound changes on the surface properties of the polymer (permeability, bondability and printability) the overall properties of the material for which it was originally chosen for remain unchanged (tensile strength). The thickness of the modified layer has been estimated to be in the range of 0 to 10 μm, depending on the conditions of the discharge (pressure, power, gas flow rate). With the inert gas as the sustaining medium, the reaction initiated in a saturated polymer, via either energy-transfer process, is thought to involve a cross-linking mechanism, in which the excited states of the polymer chain undergo homolytic bond cleavage on de-excitation, producing a wide variety of free radicals and unsaturated centers, which by radical additions produce cross links between adjacent polymer chains.

At higher power densities, ablation of small volatile chain fragments from the polymer surface cannot be discounted. However, at relatively low power loading ablation is expected to be minimal.

Clark and Dilks [36] have shown that the nature and effectiveness towards surface modification for each modes of energy transfer available through glow discharge techniques. They have used He, Ne, Ar and Kr as the inert gases for the modification of ethylene-tetrafluoroethylene by RF glow discharge. Their work indicates direct energy transfer as the prominent topmost surface modification parameter, while subsurface restructuring is affected largely through radiative energy transfer process. They have demonstrated that helium is most efficient gas for the cross linking of the outermost few monolayers whereas the cross linking of the subsurface and bulk polymer is best effected by neon.

The surface modification of PMMA films by O₂ and H₂O has been studied by Terrence et al [37] whereby they have effectively hydrolyzed a hydrophobic surface of the PMMA by glow discharge.
1.8 Humidity sensing mechanism of PMMA:

The typical water sorption isotherm in glassy polymers such as PMMA are concave in relation to the pressure axis. The dual-sorption model based on both the dissolution of solutes into a polymer and adsorption according to Langmuir’s theory in micro voids is effective for analyzing such isotherms [38-41]. However, the amount of sorbed water which was based on milligrams of sorbed water per 1g of dry PMMA, increases with an increase in RH. When this sorption isotherm appears, the swelling of the polymers and the resulting association of sorbed water molecules in the higher humidity region are suggested. Similar water sorption isotherms were observed for all PMMA films with different thicknesses. This is attributed to the water molecule’s highly condensable nature because a water molecule has a highly polar and amphiprotic structure. Hysteresis was hardly observed for these sorption isotherms. Consequently, the number of the associated sorbed water molecules seems to be small, arising from PMMA’s less hygroscopic nature [42-43]. A decrease in the amount of sorbed water with an increase in film thickness indicates an inhomogeneous water sorption in the PMMA film.

1.8.1 Basic Hypothesis of Diffusion - Mathematical Theory:

Diffusion is a process by which matter is transported from one part of a system to another as a result of random molecular motions. The transfer of heat by conduction is due to random molecular motions, and there is an obvious analogy between the two processes. This was recognized by Fick [44] who first put diffusion on a quantitative basis by adopting the mathematical equation of heat conduction derived some years earlier by Fourier [45]. The mathematical theory of diffusion in isotropic substances is therefore based on the hypothesis that the rate of transfer of diffusion substance through unit area of a section is proportional to the concentration gradient measured normal to the section:

$$ F = -D \frac{dc}{dx} $$

Where F is the rate of transfer per unit section, C the concentration of diffusing substance, x the space coordinate measured normal to the section and D is called the diffusion coefficient. In some cases, e.g. diffusion in dilute solutions, D can reasonably be taken as
constant, while in others, e.g. diffusion in high polymers; it depends very markedly on concentration. If \( F \) is the amount of material diffusing and \( C \) the concentration, both expressed in terms of the same unit of quantity, e.g. grams or gram molecules, then it is clear from the equation that \( D \) is independent of this unit and has dimensions \( \text{cm}^2 \text{ sec}^{-1} \) the negative sign in the equation arise because diffusion occurs in the direction opposite to that of increasing concentration.

It must be emphasized that the statement expressed mathematically by equation (9) is in general consistent only for an isotropic medium, whose structure and diffusion properties in the neighborhood of any point are the same relative to all directions. Because of this symmetry, the flow of diffusing substance at any point is along the normal to the surface of the constant concentration through the point.

Diffusion in a plane sheet-isotropic-is considered to be one-dimensional diffusion in a medium bounded by two parallel planes. The plane sheet is considered to be so thin that diffusing substance enters through the plane faces and a negligible amount through the edges. The solution to Fick's law for sorption is given by the equation (10). In which \( M_i \) and \( M_\infty \) are the masses of penetrate at times 't' and infinity, respectively; \( 2l \) is the thickness of the sheet; \( D \) is the diffusion coefficient.

\[
\frac{M_i}{M_\infty} = 1 - \frac{8}{\Pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{ -\frac{2(2n+1)^2\Pi^2Dt}{4l^2} \right\}
\]

Equation (10) can be simplified using Stefan's approximation to equation (11):

\[
\frac{M_i}{M_\infty} = 2 \left( \frac{Dt}{\Pi l^2} \right) \frac{1}{2} \left( \frac{1}{2} \right)
\]

From the plot of normalized capacitance Vs \( t^{1/2}/2l \) the diffusion coefficient can thus be calculated.

1.8.2 Diffusion of \( \text{H}_2\text{O} \) in \( \text{PMMA} \):

The water sorption of cross linked glassy polymers such as epoxy [46-51] and melamine-formaldehyde resins has been widely studied [52]. Considerable amount of work has also been done on the water sorption of dimethacrylate networks because of their application as dental materials. Water sorption of \( \text{PMMA} \), has also been investigated extensively by Turner D. T. [53-
where he has studied the sorption kinetics and volumetric changes together with the effects of molecular weight and cross links on water sorption in PMMA.

According to his observations PMMA of low molecular weight may take up less water than samples of normally higher molecular weight. Further he has noted that due to the addition of cross linking agents, water sorption conforms approximately to Fick’s law. The limiting water sorption is also known to increase with increase in cross links.

1.9 Polymer based Humidity Sensing methods:

Polymer sensors have been used longer than ceramic sensors beginning with devices utilizing mechanical output from dilation of hairs to synthetic polymers [56-60]. Various kinds of polymers have been used to prepare humidity sensors like cellulose acetate, polyamide and polymethyl Methacrylate. From the view point of their basic principles, they are classified into two categories. The first one is the resistive type based on the change in the electrical resistance of the material due to sorption of water vapor and the second one is the capacitive type based on the change in the dielectric constant of the material with sorption of water vapor.

These devices suffer from inaccuracy and drift due to creep. However other deficiencies also exist. For example polymers are inherently less robust than ceramics, exhibiting greater sensitivity to both thermal and chemical changes. Applications are therefore limited to lower temperatures. Slow response and hysteresis tend to be more of a problem, since the bulk polymer film must equilibrate with the atmosphere [61]. Temperature compensation is always required, since the change in capacitance with temperature is significant in comparison with its change with humidity. Nevertheless, polymers tend to be more resistant to contamination than porous ceramics, since the sensor mechanism is a bulk rather than a surface phenomenon, and device construction can be simple and less costly.

In order to improve the performance of the humidity sensor modifications in the sensor structure and the sensing material are proposed which include various chemical modifications [60] of the polymers to meet the requirement for use in basically two types of the humidity sensors, i.e. the resistive type and the capacitive type. Some of the relevant ones are described in the following sub articles.
1.9.1 Resistive type Humidity Sensors:

The polymers which are useful for the resistive type humidity sensors have a basic or acidic group such as quaternary ammonium or sulfonate group which sorbs moisture. The amount of sorbed water in the polymer correlates to the environmental humidity. Since, the electrical resistance of the polymer varies with the amount of sorbed water; the humidity can be determined by measuring the resistance or the impedance. Typical impedances recorded in this type of sensors range from 3-7.5 (log Z/Ω) in the RH range of 0–100 % [60].

In the fabrication process of these sensors a pair of gold electrodes are deposited on the polymer films to fabricate a surface type or a sandwich type of a sensor as shown in Fig-(1.8). However these hydrophilic polymers have a serious shortcoming in that they are soluble in water, so they cannot be used at higher humidities. In order to overcome these problem three methods can be used by which the polymer can be modified to make them insoluble in water. These methods are:

(i) preparation of the graft copolymer composed of a hydrophobic trunk polymer and a hydrophilic branch polymer,

(ii) cross linking of a hydrophilic polymer and

(iii) preparation of an interpenetrating polymer network (IPN) between a cross-linked hydrophilic polymer and a cross-linked hydrophobic polymer.

![Resistive type sensor diagram](image_url)

Fig-1.8: Resistive type sensor
When a hydrophilic polymer is chemically bonded on a hydrophobic polymer film by the action of γ-rays or the action of catalysts, the resultant graft polymer film sorbs water vapor but is totally insoluble in water. Such graft polymer films made of poly-tetrafluoroethylene (PTFE) and polystyrene sulfonic acid have ideal properties for humidity sensing [60-61].

When a hydrophilic polymer is cross-linked by an appropriate reaction, the polymer becomes insoluble in water [62-63]. In order to prepare a cross-linked polymer film, a solution of the hydrophilic polymer and the cross linking reagent is mixed and heated to accelerate the cross-linking reaction. After the reaction, the un-reacted materials are washed out with appropriate solvents.

An interpenetrating polymer network (IPN) technique has recently been found to be an excellent method for preparing homogeneous polymer alloys. A polymer layer composed of an interpenetrated cross-linked hydrophilic and a hydrophobic polymer can be made using this technique [64-65]. As shown in Fig-(1.9) both of the polymer networks are intermixed together so that it is insoluble in water or in any other solvent.

Y. Sakai et al [66] developed water resistant humidity sensor having a long stability by using the technique of graft polymerization. Inside a micro porous polyethylene film, 2-amylamido-2-methylpropane sulfonic acid was graft polymerized by ultraviolet irradiation. Thickness of the film and the porosity was 100 μm and 70% respectively. Gold electrodes
were deposited on both sides of this grafted film to form humidity sensor. The impedance of the sensor was measured with LCZ meter as a function of humidity with the films of various grafting ratios.

The impedance decreased four or five orders of magnitude with the relative humidity increased from 10-90%. Further at all humidities the impedance decreased with the increase in grafting ratio. Response of the sensor to step change in humidity was taken. Sakai et al[61] observed that the response time is shortened for acid containing films (< 2 W). The sensors characteristics did not show appreciable change even after 120 days indicating the long term stability.

1.9.2 Capacitive type Humidity Sensors:

In capacitive type humidity sensors hydrophobic polymers (polymers insoluble in water) are used. These polymers should have as few micro voids as possible so that the adsorbed water molecules are isolated in order not to form clusters. In these sensors cross linking is also used to modify the hydrophobic polymer to produce a sensor with small hysteresis, high selectivity and high sensitivity. The materials reported for capacitive type sensor are poly methyl methacrylate, polyvinyl cinnamate, acetylene or terminated polyimide, cellulose acetate butyrate (CAB) and polyamide have been known to be suitable material for capacitive humidity sensors[61-67].

In contrast to the resistive type of humidity sensors already mentioned above, for the capacitive type humidity sensor a thin film of a hydrophobic polymer is sandwiched between the electrodes, in which the upper electrode is usually slotted/grid type or consists of cracks for the diffusion of water vapor into the sensing polymer. The dielectric constants of these hydrophobic polymers are usually very low of about 3, when compared to that of water which is 80. When a small amount of water is sorbed by these polymers the apparent dielectric constant increases, resulting in a linear increase in the capacitance with relative humidity except for the case when the sorbed water molecule form clusters. In addition when the sorbed water forms clusters, hysteresis is observed. Consequently it is desirable to choose polymers in which the sorbed water does not form clusters. It is also required that the apparent dielectric constant is not affected by organic solvent vapors.

Although the hydrophobic polymers are insoluble in water they have some affinity for organic solvents. A capacitive type humidity sensor composed of PMMA cross linked with
divinyl monomers such as ethylene glycol dimethacrylate has been reported [68] and is found to show less hysteresis as it sorbs water much less than the cellulose derivatives. This sensor is also durable in organic solvents.

The humidity sensors have been improved by chemical modification of the polymers such as graft polymerization, cross linking (chemical means) or IPN formation so that the sensor is durable at higher humidities. Recently, plasma deposited polymer films have attracted increasing interest as materials for passivation, adhesion promotion, barrier coatings [23-69] optical waveguides [70] and relative humidity (RH) sensing applications [61,71-74].

Plasma polymerization has been used to deposit unique thin films from a variety of monomers. These monomers may or may not have a formal polymerizable structure such as a double bond, triple bond or a cyclic structure [61]. The monomer primarily acts as a source of elements to build a macromolecular structure [62]. If two monomers having different functions and elements are polymerized by plasma polymerization, the resulting film will generally contain all the elements from both the monomers. Thus, polymer films with a wide range of chemical and physical properties can be obtained easily by mixing two different monomers and plasma polymerizing. There have been several publications on the preparation, characterization and applications of thin films deposited from a single monomer by plasma polymerization [75-78].

Deposition of polymer films by plasma polymerization offers many advantages over commonly used techniques for deposition of polymer films. This is because the polymer film properties can be very easily varied or “tailored” by adjusting the plasma parameters. This technique also allows polymerization of monomer gases which do not contain reactive sites for polymerization. This is achieved by the production of active species in the plasma. The material properties can also be controlled by adjusting the plasma processing parameters like power, pressure and monomer flow rate.

Capacitive humidity sensors using PPMMA as a humidity-sensitive element have been reported by Andrew et al [79]. They have reported the role of cross linking density in the performance of the sensor. Four types of materials were basically studied: linear PMMA, PMMA cross linked with ethylene glycol dimethacrylate (EGDM), low-density plasma deposited PMMA and high-density PPMMA. They used a 13.56 MHz capacitively coupled
parallel-plate reactor. The capacitors were fabricated on silicon substrates. The PMMA dielectric lies between a solid lower electrode and a slotted upper electrode. This slotted upper electrode provides a diffusion path for water from the ambient into the PMMA. These sensors measure the changes in the dielectric permittivity of PMMA as a function of moisture content.

1.9.3 Resonant Humidity Sensor:

A third type of humidity sensing device has been recently introduced by Schroth et al [80]. Investigations in this area show that the ambient humidity has a strong influence on both the electrical as well as the mechanical properties of the polyimide polymer. In order to overcome these problems, the use of humidity induced changes of mechanical properties of polyimide have been investigated and the resonant humidity sensor has been introduced. Schroth A. et al [80] have fabricated a resonant humidity sensor based on polyimide. Their sensor consists of an oscillating square membrane, which is covered by a polyimide layer. Under the influence of humidity the layer undergoes a volume extension, which leads to a bending moment and therefore induces tensile stresses in the membrane and therefore induces tensile stresses in the membrane. Additionally, the humidity dependent bonding of hydrogen and hydroxyl molecules increases the mass of the oscillating system. Both these effects act simultaneously and cause a frequency shift.

The sensor chip is fabricated using industrial bipolar technology which allows the integration of the driving and the read-out circuit. The membrane structure is obtained by KOH etching from the back of the wafer in combination with an electrochemical etch stop at the p-n junction between the p-doped substrate and the n-doped epitaxial layer. The detection of the frequency shift as well as the thermal excitation of the oscillation is carried out by piezoresistors located at the edges of the membrane. The polyimide layer is located in the middle of the resonator membrane. It is structured by photolithography to increase the influence of the humidity induced swelling. They have further carried out simulation of the sensor behavior using FEM simulations to predict and optimize the sensitivity of the described structure. They have concluded that this sensing principle is suitable for measuring quantities of RH because it combines the advantages of a frequency measurement and
standard industrial bipolar process manufacturing and the separation between humid environment and sensor electronic.

1.10 Sensor fabrication technologies [11,81]

Sensor fabrication is one of the important tasks and various technologies are used for the same. The sensor deposition technologies affect different parameters of sensors. The advantage in science and technology offered many techniques for sensor fabrication for getting better performance. The three main fabrication technologies given as thick film, pellet and thin film. Every technique has its own merits and demerits.

1.10.1 Thick film technology [82]

Thick film technology was introduced more than 30 years ago. Generally in hybrid microelectronics thick films are preferred in which specially formulated pastes are printed onto a ceramic or insulating substrate in a definite pattern to produce a set of passive components. For formulating thick films, pastes (functional material + permanent blinder) are printed on the substrates by screen printing and fired in the belt driven furnace in air/nitrogen atmosphere by automatic process. This technology offers flexibility by a wide choice of shapes, size of components, choice of substrate material, trimming of components, easy hybridization and mass production which are useful for sensor and transducer implementation. Thickness of thick film is typically in the range of 10-30 μm.

1.10.2 Pellet formation technology [83]

Pellets are having thicknesses in the range of hundreds of μm. For pellet preparation a large amount of paste with binder is needed. The paste of the functional material is added in dye and pressure is applied on it by using hydraulic press. Thus applied pressure allows all the particles of the functional material to combine together resulting in a pellet. The strength of the pellet depends on the pressure applied. To increase the strength of pellet, generally some binders such as poly vinyl alcohol is added. The binders add strength and compactness. Binders are burnt out to neutralize their effect while subjecting the pellets for sintering. Finally electrodes are printed on both the surfaces of pellets to make them ready to use.
1.10.3 Thin film technology [84-85]

If the dimension of materials is less than or equal to mfp of electrons it is defines as thin film. The act of depositing a thin film to surface is known as thin-film deposition. The thin film is deposited atom by atom or molecule by molecule. Thin films are having many applications in industry, research and development and in daily life. The examples are anti reflecting coating, mirrors, interference filters, sun glasses, decorative coating on plastic and textiles, electronic circuits and in research. The thin film deposition is done by several processes such as physical evaporation of material in vacuum, ion plating, sputtering, electroplating, spray pyrolysis, laser ablation, spin coating, dip coating, etc. The methods of depositing thin films are briefly described in the following sub-sections.

1.10.3.1 Dip coating technology [84-85]

This is very simple type of thin film deposition technique, in which the substrate is dipped into the given solution and pulled out a uniform rate and then dried under atmospheric conditions or infrared lamp. Thus dip coated samples become ready to use. Some dip coated films like those of tin oxide have to be subjected for firing at optimized temperature and time. Reproducibility is questionable many times because of non-uniform thickness. If the solution is non-uniform in density as a depth changing then the prepared samples will be having random thickness.

1.10.3.2 Spin coating technology [84-85]

Spin coating is used to get uniform thin films on flat substrate. A predetermined amount of solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. Rotation is continued while the fluid spin off the edges of the substrate, until the desired thickness of film is achieved. The applied solvent used is usually volatile, and simultaneously evaporates. Higher angular speed of spinning results in thinner films. The thickness of the film also depends on the concentration of the solution and the solvent.

1.10.4 Deposition technologies [81,84-85]

In CVD chemically reacting volatile compound of a material is deposited in the presence of other gas to produce a nonvolatile solid which deposits on the substrate. The high temperature CVD is having many applications in several many fields.
Physical deposition uses mechanical or thermodynamic means to produce a thin film of solid. An everyday example is the formation of frost. Since most engineering materials are held together by relatively high energies, and chemical reactions are not used to store these energies, commercial physical deposition systems used to require a low-pressure environment to function properly. The material to be deposited is placed in an energetic, entropic environment, so that particles of material escape its surface. Facing this source is a cooler surface which draws energy from this particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particles to travel as freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal.

Sputtering relies on a plasma (usually a noble gases, such as argon) to knock material from a “target” a few atoms at a time. The target can be kept at relatively low temperatures, since the process is not one of evaporation, making this one of the most flexible deposition techniques. It is especially useful for compounds or mixtures, where different component would otherwise tend to evaporate at different rates. The sputtering step coverage is more or less conformal.

Thermal decomposition of gaseous species such as hydrides, carbonyls and organometallic compounds on temperature control substrate is called spray pyrolysis.

1.11 Literature Review

Y. Sakai et al [66] developed water resistant humidity sensor having a long stability by using the technique of graft polymerization. Inside a micro porous polyethylene film, 2-amylamido-2-methylpropane sulfonic acid was graft polymerized by ultraviolet irradiation. Thickness of the film and the porosity was 100 μm and 70% respectively. Gold electrodes were deposited on both sides of this grafted film to form humidity sensor. The impedance of the sensor was measured with LCZ meter as a function of humidity with the films of various grafting ratios.

The impedance decreased four or five orders of magnitude with the relative humidity increased from 10-90%. Further at all humidities the impedance decreased with the increase in grafting ratio. Response of the sensor to step change in humidity was taken. Sakai et al observed that the response time is shortened for acid containing films (< 2 W). The sensors characteristics did not show appreciable change even after 120 days indicating the long term stability.

Y. Sakai et al [66] have reviewed the work of the last 10 years (1986-96) about studies on humidity sensors fabricated with organic polymers. Both the resistive and capacitive type of
sensors are reviewed. They have concluded that in order to fabricate humidity sensors using polymeric materials, one must modify the polymers by chemical reactions to meet the requirements for reliable humidity sensors. Several methods useful for improving the characteristics of humidity sensors are available in the literature. In case of resistive type of sensor one must modify the hydrophilic polymer to be insoluble in water while still maintaining the hydrophilic character to adsorb sufficient water molecules to form an ionic conduction path. Cross linking or graft polymerization is a promising solution to this problem. Sakai et al [67] have proposed several one step procedures for this purpose. T. Maddanimath et al [86] have fabricated a resistive type humidity sensor by using surface modified polyethylene (PE) and polypropylene (PP). The surface fictionalization of the polymer was done by dipping the polymer films in oleum for different time intervals at ambient conditions and later washed in de-ionized water. They have shown that controlled sulphonation have promising humidity dependent resistance changes ($10^9-10^9$Ω with change in the RH from 30 to 95%) and also other favorable characteristics such as linearity and short response time. They have carried out systematic study of humidity sensing behavior with and without different types of surface fictionalization, where in it is noted that the sensitivity is controlled by surface structure and the extent of functionalization, causing a change in carrier concentration and the mobility of the protons and counter ions.

Y. Li et al [87] have prepared resistive humidity sensors using polymer solid electrolytes. Monolayer and bilayer devices were prepared by filming polymer electrolytes or blends of polymer electrolytes on interdigitated gold electrodes. They tested the electrical characteristics of the devices as a function of %RH in a home made cell equipped with a commercial humidity sensor. Different values of %RH were obtained by bubbling dry argon through water. The impedance was measured for corresponding %RH. The logarithm of the impedance modulus or the resistance gave straight lines, as a function of %RH, only for some devices based on copolymers or polymer blends. They have concluded that by utilizing mono or bilayer structures of polymers or copolymers and empirically choosing the more appropriate working frequency, suitable conditions for a good humidity sensing device construction can be found. Andrew et al [79] characterized the frequency dependent response of the films to moisture from 12 Hz to 100 Hz. A β relaxation was identified in the linear and cross linked PMMA films, but was observed to be absent in the plasma-deposited films. This result they have interpreted as
indicating that the high density of cross links in the plasma deposited films inhibits segmental motion in these films. The sensitivity of their PPMMA sensors at 100 Hz was about 60% of the linear and the cross linked PMMA. The hysteresis was found to be low above 1 kHz. The cross linked PMMA however is reported to exhibit significant hysteresis below 1 kHz. The response to moisture at 100 kHz is most linear for the plasma deposited films. The sensitivity measured for these sensors was 2 pF/%RH.

In order to minimize the hysteresis and to increase the sensitivity of humidity sensors, Chan et al [88] have used porous polyamide to fabricate capacitive humidity sensor. The polyamide selected contains weak hydrophilic carbonyl group which is suitable for increasing the sensitivity. They deposited the polyamide sensing layer by spin coating polyamic acid onto the lower Ti electrode (1500 Å thick) patterned by e-beam evaporation on an oxidized Si substrate. The coating was cured at a temperature up to 45 °C in argon environment. In order to avoid shorting Al2O3 was deposited on to the lower Ti electrode. To increase the sensitivity, cracks were generated in the top electrode and the polymer layer. To generate cracks on the sensor structure, they deposited the upper chromium electrode in a state of tensile stress using e-beam evaporation. The width and size of the cracks were increased with the thickness of the upper electrode. Chan et al [88] have suggested that if the polymer humidity-sensing layer is too dense or hard, the sensor’s sensitivity becomes very low and the upper electrode should be porous for water molecules to pass through and reach the sensing layer. The sensor sensitivity they have reported in the 10-90 %RH range is 0.25 pF/%RH, increasing with relative humidity. The hysteresis was observed in the humidity range 3 %RH at 50 %RH. They have attributed this to the hydration and dehydration processes.

Matsuguchi M. et al [89] have worked on the stability and reliability of capacitive-type relative humidity sensor using cross linked polyimide films. They have used cross linked polyimide (C-PI) and cross linked fluorinated polyimide (C-FPI) as the sensing material in a sandwich type sensor element. They observed that the electrical capacitance changed linearly over 10-90% RH, their hysteresis was less. Their C-FPI sensor demonstrated long-term stability in harsh environments and the drift was as small as +1.1 pF after 1000 hr of exposure to 40 °C temperature at 90 %RH atmosphere. The C-PI sensor proved to be resistant to chemicals. The sensor output was not affected even after exposing the sensor elements to saturated acetone.
vapor for 20 min. They have concluded that a stable and reliable sensor usable in an office building and in a factory can be achieved by using these sensors properly.

Matsuguchi et al [90] have prepared cross linked PVCA on a substrate using photo irradiation technique and have evaluated them as a capacitive humidity sensor. The excitation wavelength is shorter than 325 nm. The effect of irradiation conditions on the degree of cross linking and also on the sensing characteristic was examined. In addition the adsorption behavior of various polar organic vapors was also studied. The device structure in this case is a sandwich type of sensor. Platinum thin film was used as a lower electrode and gold film as an upper electrode. To measure the amount of adsorbed solute the film was prepared on AJ–cut quartz crystal. The electrical properties were measured using an LCZ meter. The humidity was varied by controlling the ratio of dry and water saturated air. The response time was less than 30 sec. in humidification process and was slightly higher in the desiccation process. This also depended on the degree of cross linking. The degree of cross linking was determined from the dielectric loss measurement and the FTIR analysis.

It was found that as the photo irradiation time increases the magnitude of the relaxation peak reduced and shifted to a higher temperature side. It is known that the dielectric relaxation of a polymer arises from the segmental motion of the main chain and the side chain. If the cross linking reaction has taken place then the film becomes rigid and the segmental motion of the main chain is depressed and as a consequence the dielectric loss is lowered. Therefore, lowering of dielectric loss confirms the formation of cross links. In this case, the cross linking reaction proceeded with increase in the irradiation time. The cross linking degree was also confirmed by FTIR analysis 90% cross linking was reached within 4 hrs of irradiation.

The humidity response of the PVCA films was measured at 30 °C in terms of the ratio of capacitance at certain %RH and capacitance at 0 %RH. The ratio was found to increase linearly with humidity. The sensitivity was seen to have been enhanced with photo irradiation time. The maximum ratio observed was 1.2 at 90% humidity for 4 hr irradiated sample. From the results of the amount of adsorbed water at a particular humidity and the degree of cross linking, the authors postulated that the enhancement of water absorption ability is related to the decomposition of the polymer by exposure to UV light. Reports are also available that the saturation value for water uptake of the cross linked PMMA with dimethylacrylate monomers increases with an increase in the degree of polymerization.
Jose M. et al [91] have for the first time developed a capacitive humidity sensor using poly (ethyleneterephthalate)-PETT as the dielectric. They have fabricated a sandwich type of a sensor by cutting 50 µm PETT films in about 1 cm diameter circles on which metallic gold thin film (0.1-0.3 nm thick) was deposited by magnetron sputtering. Electrical contacts were made by nickel contacts. This device was incorporated in an oscillator circuit to use it as a humidity sensor. This sensor enabled them to measure the humidity between 10-97 %RH range over saturated salt solutions. They have concluded that the accuracy of their sensor was about ± 2 %RH in the complete measurement range. Its response time was found to be comparable to those of the commercial sensors and has good stability over time.

Li Y. et al [87] have carried out work on capacitive sensors using polymer solid electrolytes. They have used monolayer and bilayer devices prepared by filming polymer electrolytes/blends of polymer electrolytes on interdigitated gold electrodes similar to the ones used for resistive type of sensor as mentioned above. They measured the variation of capacitance with %RH at a constant temperature 22 °C. The measured capacitance in linear or logarithmic scale gave a linear trend with %RH. They have concluded that these devices give fast response and operate over a wide range of %RH.

P.R. Story et. al. [1] reported study of low-cost sensors for measuring low relative humidity. The performance of low-cost commercially available (five different) capacitive and resistive type polymeric humidity sensors has been compared to that of prototype thick- and thin-film polyimide based sensors. Both capacitive and surface acoustic wave (SAW) sensing mechanisms have been studied for the thin-film structure. The prototype sensors were optimized for improved performance at low relative humidity (RH). The commercial capacitive microsensors have a linear response in the range 5-95% RH. The resistive sensors are found to be non linear. The prototype thick-film sensor has a non-linear response, while the response of the thin-film prototype sensor is comparable to that of the commercial capacitive microsensors. The SAW sensor has the potential for higher sensitivity than the commercial capacitive microsensors, but is less linear.

Two prototype capacitive humidity sensors were also studied. They included both thick- and thin-film interdigitated electrode designs as shown in Fig. 1(a) and (b). The thick-film sensor was fabricated with 18 (0.65 mm wide) finger pairs spaced 0.65 mm apart on a 2 in X 2 in alumina substrate using standard screen-printing processes. The thick-film conductor, which had a final
thickness of 23 μm, was Pd/Ag. The thin-film design was photolithographically patterned aluminum 150 nm thick on a quartz substrate. The pattern consisted of 90 (10 μm wide) finger pairs spaced 10 μm apart. A 2 μm polyimide film (DuPont Pyralin 2555) was spin coated at 5000 rpm for 60 s on both substrates. The samples were softbaked at 120 °C for 10 min and cured at 350 °C for 30 min in nitrogen.

Authors found that capacitive type thin-film sensor had a fairly linear response with some hysteresis at higher RH. Further they found that the total percentage change in capacitance for the thick-film sensor was greater than that of the thin-film sensor and the thick-film sensor showed no response below 40% RH. They have attributed this to the microscopic structures of these two sensors. The polyimide film is much thicker (2 μm) than the electrodes (150 nm) on the thin-film sensor, therefore the electric field between the electrodes can be considered to be entirely most of the electric field is assumed to be in the air gap between the electrodes. In case of thick electrodes the polyimide (2 μm) is much thinner than the thick film electrodes (23 μm). A smaller overall response would therefore be expected for the thick-film sensor. This only occurred at low RH. The reason for the large capacitance change at high RH is not provided.

Y. Sakai et al [92] have presented review on the humidity sensors fabricated with organic polymers. Several useful methods for improving the characteristics of humidity sensors based on polymers are proposed. In the case of a resistive-type sensor, cross-linking of hydrophilic polymers or formation of interpenetrated polymer networks with a hydrophobic polymer makes the hydrophilic polymers durable at high humidities. Graft polymerization is another method of preparing water-resistant humidity sensors. In the case of capacitive-type sensors, cross-linking is also useful to modify the hydrophobic polymer to produce a sensor with small hysteresis, high selectivity and high sensitivity.

Polymers insoluble in water - hydrophobic - have been used to fabricate capacitive-type humidity sensors. Cellulose acetate butyrate (CAB) and polyimide have been known to be suitable materials for capacitive humidity sensors. However, many problems such as hysteresis, stability at high humidity’s and at high temperature and durability on exposure to some kinds of organic vapors still remain to be solved. To complete the capacitive-type humidity sensor for practical use, it is important to elucidate the sensing mechanism of this type of sensor. Authors have examined the correlation between the permittivity and the amount of sorbed water for the various cellulose derivatives in one of their previous papers. The hysteresis was confirmed to be
caused by the formation of clusters of sorbed water molecules. It was found that the polymer should have as few microvoids as possible so that the adsorbed water molecules are isolated in order not to form clusters. The formation of clusters leads to appreciable hysteresis. In some cases cross-linking of the polymer chains was found to depress the clustering of water. In addition, the cross-linked polymers are durable in the presence of organic vapors.

Authors reported poly(methyl methacrylate) (PMMA) PMMA sorbs a smaller amount of water than CAB and other cellulose derivatives, resulting in less opportunity to form clusters. The hysteresis for a PMMA capacitive-type humidity sensor is therefore less than ±1% RH, which is smaller than that of the conventional sensors. In addition, cross-linking of PMMA was carried out using divinylbenzene or ethylene glycol dimethacrylate. Authors report that the cross-linking of PMMA reduced the hysteresis and the temperature coefficient. The durability in the presence of organic vapors was also much improved. Authors also have reported Acetylene-terminated polyimide and Poly(vinyl cinnamate) as humidity sensors.

P.M. Harrey et al [4 ] reported work on Capacitive-type humidity sensors fabricated using the offset lithographic printing process. Authors used polyimide and polyethersulphone (PES) as humidity sensitive materials.

Printed humidity sensors were fabricated via the conductive lithographic film (CLF) process and evaluated. polyimide and polyethersulphone (PES) were investigated as humidity sensor films. A standard sheet-fed lithographic printing press (Heidelberg GTO46) was used to print the electrodes of the sensor structures. Printed sensors were formed on 25 mm PES, and three different thickness grades of polyimide film: HN30, HN50 and HN100 (thicknesses of 7.6, 12.5 and 25 mm, respectively. In addition, sensors with patterned electrode films which incorporate micro-pores were also fabricated and evaluated.

For comparative purposes, a thin film sensor was also formed on polyimide HN film. The sensor was fabricated by sputter coating gold electrode films onto opposing sides of the 7.6 mm polymer film. The calculated thickness of the electrode films was 600 A° (0.06 μm). This sensor was used to compare the response times of the experimental printed sensors to a more conventional thin-film electrode sensor. Electrical testing of the sensors was accomplished by bonding silver wire test leads to the electrode films of the sensors using a silver loaded conductive adhesive. The effective overlap area of the sensor is 200 mm². Humidity tests were performed using a Vaportron H100 humidity test chamber.
The capacitance of the structures was measured using a Fluke PM3606 LCR meter (1 MHz and 1 V test signal). The capacitance response of the sensors was studied over the range of 10–90% RH. Both sensors responded linearly to changes in relative humidity. The results indicate that the sensors exhibited similar nominal capacitances (235 pF). The polyimide sensor exhibited a greater change in capacitance than the PES sensor over the measured range of 10–90% RH. These findings are in accordance with manufacturers specifications which detail Kapton HN film polyimide as having a greater moisture absorption capacity than PES film (2.8% compared to 2.2% ASTM D-570-98).

The capacitance change (pF) and sensitivity (pF/%RH) of the sensors was shown to be inversely proportional to the sensing film thickness. The thin (7.6 μm) polyimide film sensor demonstrated a sensitivity of ~1 pF/% RH, this is 2–3 times greater than contemporary commercial capacitive-type sensors. It has also been shown that the response time of the sensor is inversely proportional to the thickness of the polymer sensing film. Polyimide sensors formed on 25, 12.5 and 7.6 μm film exhibited response times ($t_{63}$) of 10.5, 5.0 and 1.8 min, respectively. Comparatively, PES sensors were shown to respond more quickly than equivalent film thickness polyimide sensors.

Pi-Guey Su et al [7] have worked on resistive type humidity sensors based on PMMA. The ionic conductivity of PMMA was modified by doping with two different salts KOH and K2CO3. These dopants are having largely different dissociation constants. The electrical properties of PMMA doped with different amounts of KOH or a mixture of KOH and K2CO3 were examined in detail as a function of relative humidity (RH), to elucidate the contribution of the salts to the sensing properties (linearity and sensitivity).

The sensors were fabricated by dip-coating and subsequent in situ co-polymerization on an alumina substrate with a pair of comb-like electrodes. The precursor solutions were prepared from methyl methacrylate (MMA, 99%, Acros Corp.), KOH (99%, Aldrich) and K2CO3 (99%, Aldrich). The two inorganic salts were mixed into MMA at different compositions together with a small amount of ethanol as an interface modifier. Then, the alumina substrates were coated with the precursor solutions and were in situ co-polymerized in an oven at 90 °C for 1 h to give PMMA-based humidity sensors.

Complex impedance of a sensor was measured with an LCR meter (Philips PM6304) in a test chamber at measurement frequency of 1 kHz, an applied voltage of 1V, an ambient
temperature of 25 °C and different humidity levels in the range of 30–90%RH. The humidity in the test chamber was controlled by mixing dry and wet air through mass flow controllers. The RH values were measured with a calibrated hygrometer (Rotronic) with an accuracy of ±0.1%RH. Sensitivity is defined as the slope of logarithmic impedance (log Z) versus %RH and linearity in terms of correlation coefficient is defined as the R-squared value of the linear fitting curve in the range from 30 to 90%RH.

Authors reported that pure PMMA exhibited only a little impedance change in the humidity range studied. They attributed it to its hydrophobic property. When the PMMA was doped with KOH, an inverse sigmoidal humidity dependence of the logarithmic impedance was observed at both low and high dosage. The sensitivity (slope) increased from 0.0012 to 0.0638 with the KOH doping. However, the impedance change was observed at 30–60%RH and more notably at 50–60%RH, and almost no impedance change in the range of 60–90%RH.

The PMMA doped only with KOH had a high sensitivity but low linearity. The poor linearity of the PMMA/KOH complex was improved by further doping of K2CO3. The PMMA doped with a mixture of KOH (0.6%, w/w) and K2CO3 (0.6%, w/w) was optimal in both sensitivity and linearity in the range of 30–90%RH.

With simultaneous doping with KOH and K2CO3, the linearity increased with increasing the dosage of K2CO3. However, the sensitivity decreased with increasing the dosage of K2CO3. The impedance continuously decreased along with the humidity increase in the range of 30–60%RH, though the impedance values increased with increasing the dosage of K2CO3 at 60–90%RH. This behavior is thought to be due to aggregations of ions at high concentrations.

In order to explain the results of the PMMA/KOH/K2CO3 polymer–salts complexes, authors discussed the mechanism for the conductance variation with %RH in the following way. With the absorption of water, a sort of thin liquid layer forms around the polymer chains or fills the openings in the sensing polymer films through capillary condensation or swelling. The sorbed water enhances the electrolytic dissociation of the inorganic salts in the polymer–salts complexes. Finally, the sorbed water acts as a plasticizer which gives rise to an increase in mobility of the ions dissociated.

It is well known that KOH has a very high dissociation constant (6.63×10¹⁰) and therefore it is easily and completely dissociated under the conditions of low humidity. Compared with KOH, the dissociation constant (1.50) of K2CO3 is quite low. It means that the K2CO3 can
be dissociated completely only under the conditions of highly humid atmosphere. Thus, it is important to incorporate both KOH and K2CO3 into the PMMA-based composites for the wide-range humidity detection.

In order to get higher sensitivity and better linearity of the PMMA/KOH/K2CO3 materials in a wider humidity range, the optimum doping ratio of KOH to K2CO3 was investigated. It was found that the PMMA doped with a mixture of KOH (0.6%, w/w) and K2CO3 (0.6%, w/w) was optimal in both sensitivity and linearity in the range of 30–90%RH. The sample prepared at optimum conditions was further tested for evaluation of hysteresis and stability. The hysteresis was evaluated by the percent difference in logarithmic impedance between humidification and desiccation processes, that is, by $100 \times (\log Z_{\text{desic}} - \log Z_{\text{humid}})/\log Z_{\text{desic}}$ at 60%RH. The hysteresis was within 4%RH at most. Moreover, the stability test, where a sensor was subjected to repeated humidification and desiccation cycles more than 50 times in the range of 30–90%RH at 25 °C, indicated that the present humidity sensors worked normally during the test.

Masanobu Matsuguchi et al [6] reported a capacitive-type humidity sensor based on a poly(methyl methacrylate) (PMMA) cross-linked with divinylbenzene (DVB). They examined the influence of introducing a cross-linked structure in the sensing polymer on the long-term stability of the sensor in a hot and humid atmosphere. As the DVB content increased, the irreversible increase in the water sorption ability of the cross-linked PMMA by long-term aging in a 40°C and 90% RH atmosphere was depressed. This was because the irreversible increase in volume of the sensing polymer caused by swelling in such atmosphere was prevented due to the rigid cross-linked structure. The depression of the drift of the water sorption ability resulted in the depression of the drift of the sensor capacitance.

Sandwich-type devices were prepared for dielectric measurement. Methyl methacrylate (MMA) monomer was mixed with divinylbenzene at various weight ratios and polymerized with benzoyl peroxide until the mixture reached the appropriate viscosity, followed by spin coating on a 4 in. alumina substrate with a Pt lower electrode. The coated thin film was heated to achieve complete polymerization at 80 °C for 24 h in a N2 atmosphere. The thickness was varied by changing the rotational speed of the spin-coater. Finally, a gold upper electrode was deposited by vacuum evaporation technique. To measure the amount of sorbed water, the cross-linked PMMA film was also coated on a quartz crystal oscillating element (4 MHz) having a silver electrode.
plated on both sides. The relative humidity (% RH) of which was controlled by mixing dry and wet air. The measurement was carried out at 100 kHz with an LCZ meter.

The aging test the devices were placed in a humidistat in which the atmosphere was maintained at 40 °C and 90% RH. Each device was occasionally removed from the humidistat, and the humidity dependence of the device’s characteristics was measured over a humidity cycle of 10-90% RH at 30 °C. After the measurement, the device was returned to the humidistat. These procedures were then repeated.

It was found that the depression of a capacitive-type humidity sensor’s drift by long-term aging in a hot and humid atmosphere was achieved by introducing a cross-linked structure in the sensing polymer. The sensor’s drift was smaller for the cross-linked PMMA having a larger DVB content, corresponding to a smaller change in the water sorption ability. The effect of cross-linking on the drift was explained by the depression of the irreversible increase in volume of the sensing polymer caused by swelling of the PMMA by aging. The cross-linking technique may also improve the chemical resistance of the sensing polymer in wet and humid atmosphere; however, very little information is currently available for such discussion.

In addition, it was shown that the drift of the sensor based on the cross-linked PMMA was observed only in the early aging period. This result means that long-term stability can be achieved in a capacitive humidity sensor, even in a hot and humid atmosphere, by the pretreatment of the present sensor once in such an atmosphere before use. Zhi Chen and Chi Lu have reported review of Materials and Mechanisms of Humidity Sensors. The review is based on various materials for both relative and absolute humidity, including ceramic, semiconducting, and polymer materials. Extract of the review on polymer materials, only is reported here.

Most of the polymers are carbon-hydride compounds or their derivatives. The carbon atoms link each other one by one, either by sigma bond (single bond) or sigma bond plus pi bond (double bonds or triple bonds), forming a long chain, which is called the backbone of the polymer. Functional groups are rooted on the backbone, which could be either single atoms (e.g., oxygen or halogen) or molecular groups (e.g., –COOH, –NO2). The functional groups, along with the basic structure of the backbone, determine the chemical and physical properties of the polymers. Polymeric humidity sensors have been widely studied in research and applied in industry for more than 30 years. Most of the sensors are based on porous polymer films thinner
than millimeters and their sensing principle is quite similar to that of ceramic sensors. The film is filled with micro-pores for water vapor condensation and some of the measurable physical properties change due to the water absorption.

The mechanism of protonic conduction inside the adsorbed water layers on the surface of the sensing materials was discovered in study of TiO2 and a-Fe2O3. As shown in Figure 3, at the first stage of adsorption, a water molecule is chemically adsorbed on an activated site (a) to form an adsorption complex (b), which subsequently transfers to surface hydroxyl groups (c). Then, another water molecule comes to be adsorbed through hydrogen bonding on the two neighboring hydroxyl groups as shown in (d). The top water molecule condensed cannot move freely due to the restriction from the two hydrogen bonding (Fig. 3(d)). Thus this layer or the first physically-adsorbed layer is immobile and there are no hydrogen bonds formed between the water molecules in this layer.

As water continues to condense on the surface of the ceramic, an extra layer on top of the first physically adsorbed layer forms (Fig. 4). This layer is less ordered than the first physically-adsorbed. For example, there may be only one hydrogen bond locally. If more layers condense, the ordering from the initial surface may gradually disappear and protons may have more and more freedom to move inside the condensed water through the Grotthuss mechanism. In other words, from the second physisorbed layer, water molecules become mobile and finally almost identical to the bulk liquid water, and the Grotthuss mechanism becomes dominant. This mechanism indicates that sensors based purely on water-phase protonic conduction would not be quite sensitive to low humidity, at which the water vapor could rarely form continuous mobile layers on the sensor surface. The two immobile layers, the chemisorbed and the first physisorbed ones, while cannot contribute to protonconducting activity, could provide electron tunneling between donor water sites. The tunnelling effect, along with the energy induced by the surface anions, facilitates electrons to hop along the surface that is covered by the immobile layers and therefore contributes to the conductivity. This mechanism is quite helpful for detecting low humidity levels, at which there is not effective protonic conduction.

According to sensing mechanisms, polymeric humidity sensors are divided into two fundamental categories: resistive-type and capacitive-type. The former responds to moisture variation by changing its conductivity while the latter responds to water vapor by varying its dielectric constant. Almost all of the humidity sensors based on polymers operate at room
temperature, due to polymers' high sensitivity to heat. Copolymers and mutually reactive copolymers have also been studied for humidity sensing. Polymeric humidity sensors based on piezoresistive, surface wave acoustic (SAW) devices and Optical measurements are also studied. Polymeric resistive humidity sensors are based on two types of materials: polyelectrolytes and conjugated polymers.

Polyelectrolytes are hydrophilic or even water soluble while conjugated polymers are rather hydrophobic and unable to absorb much water.

Polyelectrolytes are polymers with electrolytic groups, which could be salts, acids, and bases. Based on functional groups, humidity-sensitive polyelectrolytes can be fundamentally divided into three major categories: quaternary ammonium salts, sulfonate salts, and phosphonium salts.

Fuke M.V. et al [3] have worked on the evaluation of Co-Polyaniline nanocomposite thin films as humidity sensor. Polyaniline is unique among the known conducting polymers because its conductivity is controlled by the doping levels of oxidation and protons. Oxidation states of polyaniline, whose electrical properties are sensitive to water, provide a basis for potential applications in sensors for humidity control. The aqueous environment changes the conductivity due to two reasons:

1. Adsorbed water molecules dissociate at imine nitrogen centers.
2. Positive charge migrates through the polymer.

Spin coated films of Co-Polyaniline nanocomposite are evaluated for their transmission properties using He–Ne laser for humidity sensing. The thickness (17–29_m) of the films is varied by multiple deposition of Co-Polyaniline nanocomposite on a glass substrate. The samples exhibit typically two to three regions in their sensitivity curve when tested in the relative
humidity (RH) range of 20–95%. The sensitivity ranges from 0.1 mV/%RH to 12.26 mV/%RH for lower to higher thickness. The sensors show quick response of 8 s (20–95%RH), and a recovery time of 1 min (95–20%RH) with good repeatability, reproducibility and low hysteresis effect. The sensitivity of the sensor increases with humidity and thickness. Material characterization is done by X-ray diffraction (XRD), scanning electron micrograph (SEM) and Fourier transform infra-red spectroscopy (FTIR).

All the sensors roughly exhibit three regions of sensitivity with very low sensitivity at low humidity levels, increased sensitivity at medium humidity levels and high sensitivity at the high humidity levels. At the thickness of 23.57 μm the maximum sensitivity is seen. As the relative
humidity increases the output voltage decreases. At a lower humidity (20 to 40 RH%) the layer of hydroxyl groups is formed [93]. The water vapor molecules are chemisorbed through a dissociative mechanism by which two surface hydroxyl groups per water molecule are formed. This does not change the transmission of light through the film. Therefore at lower relative humidity the sensor response is poor. At a higher humidity (60 to 80 RH%) the water molecules get adsorbed on the wall of the pores. The light through the film gets absorbed in proportion to the deposition of water molecules on the pore walls, in turn the output voltage decreases. For all the samples at higher humidity, around 80%RH, switching behavior is exhibited because of formation of water meniscus on the film, which absorbs the incident light making transmitted intensity to be small.

The variation of humidity response i.e decrease in the output voltage with increase in the relative humidity is also attributed to the mobility of Co ions which are loosely attached to the polymer by weak Van der Waals' forces of attraction. Authors have taken the SEM images of the films. They have reported that lower thicknesses have higher porosity and hence give higher sensitivity. Authors further found out that the hysteresis for 23.57μm thickness is 1%. And the response and recovery time of the sensor is given as 8 s and 1min, respectively. The repeatability and the reproducibility of the optical humidity sensor using Co-Polyaniline nanocomposite was found to be very encouraging for all the concentrations for 23.57μm.

1.11 Aims and objectives:

The main aim of this research was to deposit and/or treat the selected material - polymethyl methacrylate - by plasma processes and compare their performances as capacitive type humidity sensors.

The main objectives of the study were –

- Study and prepare the experimental set ups for plasma treatment, plasma polymerization and spin coating of thin and thick films.
- Formation of thick/thin film on the substrate using selected material.
- Synthesize the materials by plasma polymerization and plasma treatment of spin coated polymers.
- Structural & physical characterization of synthesized polymers by techniques such as gravimetric method, taly step method, FTIR, SEM…etc.
- Fabrication of capacitive type humidity sensors.
• Determination of sensitivity, response time, recovery time, hysteresis, reproducibility, repeatability of capacitive type sensor.
• Study and specify characteristics of fabricated sensors using above mentioned techniques.
• Study the optical properties of PMMA. For that study drop casted and spin coated films of PMMA were used.
• Compare the characteristics of sensors fabricated using different methods and conclude accordingly.
• Comparison of the obtained results with the ones available in the literature.

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