CHAPTER - 2

EXPERIMENTAL DETAILS
2.1 **FILM PREPARATION TECHNIQUES** :-

Materials can be casted into films by thermal evaporation (159), sputtering (160), and chemical deposition methods (161). In thermal evaporation, solid materials vaporize when heated to sufficiently high temperature. The condensation of vapour on to a cooler substrate yields films. Evaporation can be carried out by a flash, arc and laser or by resistive, exploding wire, RF and electron bombardment heating. The ejection of atoms from the surface of the material by bombardment with energetic particles is called sputtering. If ejection is due to positive ion bombardment, it is referred to as cathodic sputtering. The sputtered atoms can be condensed on a substrate to form a film. Because of the high pressure of the gas used and high sensitivity to contamination is commonly used glow discharge sputtering, the technique has generally been termed dirty. Sputtering can be achieved by low pressure, RF, ion beam and reactive sputtering. Electro and electroless deposition and anodic oxidation are chemical methods to deposit films. In chemical vapour deposition technique, a volatile compound of the substance which is to be deposited, is vaporized. The vapour in thermally decomposed or reacted with other gases, vapours of liquids at the substrate to yield non volatile reaction products which deposit atomistically on the substrate. Technology of film preparation has been reviewed by chopra (162).

The irradiation technique for the preparation of polymer films is
a high energy technique. Similarly RF sputtering of polymers is also a high energy process. In these high energy processes the cross linking of the polymer chains is highly probable. The films so formed show high dielectric losses and degradation with time. These films are, therefore, not suitable for practical applications. Films of polyvinylchloride acetate co-polymer (163) have been prepared by spreading cyclohexanone solution of the polymer over a water surface. Spivack (164) has prepared parylene (the generic name of a family of polymers based on poly-p-xylene) films by using the vapour phase deposition process which has been described by Gorham (165). The films thus formed have excellent mechanical, physical, electrical and barrier properties. They are virtually inert to most acids and bases and are insoluble in most organic solvents below 170°C. The isothermal immersion technique (166, 167) on the other hand, appears to be simple and powerful technique for obtaining durable and useful polymer films. Isothermal immersion technique has been used by several workers (168, 169) to prepare polymer films. In this method, the growth of the molecular chains on the substrate is predominantly lateral. The molecular chains or the clusters of the chains observed on the substrate attain a definite equilibrium size. These clusters do not significantly increase in size as the equilibrium thickness of the film increases or their number increases. The clusters tend to deform in one particular direction and the extent of deformation increases as the equilibrium film thickness increases. The clusters of the molecular chains have a preferred direction of orientation. Films of higher equilibrium thickness have more

Fig 2.1 ISOTHERMAL IMMERSION APPARATUS
of amorphous areas surrounding the crystalline area.

It is clear from what has been stated above that the growth of the films from solution occurs by absorption controlled nucleation of molecular chains on the substrate and the further growth occurs by the attachment of more chains on the already adsorbed chains forming a cluster of chains. The adsorbed chains and subsequently the clusters of chains adjust themselves laterally on the substrate.

2.2 **FILM PREPARATION :-**

Commercial grade PS was used in the work. PS was dissolved in cyclohexanone. Pyrene was also dissolved in cyclohexanone. Pyrene solution was mixed in PS solution to have dopant concentrations 0.1, 0.5, 0.8, 1, 2, 3 and 5 g/l. This method of doping in which pyrene solution is mixed in PS solution is termed common solvent method. Al foils were cleaned by rubbing them with cotton and then by keeping them immersed in benzene. The cleaned foils were stored in pure alcohol. Isothermal solution immersion growth technique of preparing the films involves isothermal immersion of the substrate in to the polymer solution held at a particular temperature for a certain time. The apparatus used to prepare the films is shown diagrammatically in Fig.- 2.1.

Polymer solution was immersed in the oil bath. The temperature of the oil bath was kept constant at 30°C. The substrate was held in the constant temperature bath. After bringing the solution and the substrate at 30°C, the substrate was immersed in the solution for 10 minutes. The films were dried by keeping them within the thermostat at 30°C more than
Fig: 2.2 Electrode Assembly

Fig: 2.3 Assembly for Photo experiment
2.3 **EVALUATION OF FILM THICKNESS** :-

The thickness of the film was extrapolated by measuring its capacitance at 10KHz and taking the permittivity ($\varepsilon$) value equal to 3.

2.4 **VARIATION OF ELECTRODE FORMING MATERIAL** :-

Films were grown on Al substrates. To study the electrode effect, films were also grown on Zn, Ni and Cu substrates. The substrate acted as an electrode and the other of Al $1\text{cm}^2$ in area was pressed on to the film.

2.5 **ELECTRODE ASSEMBLY** :-

A pressed on electrode assembly was used in the investigation. It is diagrammatically shown in Fig 2.2. The film along with the substrate was kept on the bottom teflon sheet so that the substrate contacted with the teflon. An Al electrode of $1\text{cm}^2$ in area surrounded with the guardring to avoid the surface effects was pressed on the film with the help of the flyscrew. The contact of the flyscrew with the electrode was insulated with a teflon disk. The substrate acted as another electrode.

2.6 **ASSEMBLY FOR PHOTO EXPERIMENT** :-

Assembly used in photo-polarization and depolarization experiment is schematically shown in fig-2.3. UV light of wavelength 1518 $\text{A}^\circ$ from a 15 watt lamp was incident on the film through a semi-transparent silver electrode. The substrate acted as the other electrode.

2.7 **ROLE OF AIR IN THE PRESENT EXPERIMENTAL SETUP** :-

For fundamental studies vacuum deposited electrodes are preferable. However, in the present investigation pressed on electrodes
have been used. In case of pressed on electrodes the contact between the electrodes and the polymer is imperfect and there are air spaces between them, in which at high field strengths Townsend breakdown will occur, so that ions or electrons from the air are injected into the polymer. The homo-charging by breakdown of the air is deliberately intensified in the manufacture of electrets (170). This development is logical, because the deposition of homo charges from the air is a much faster process than the hetero charging by dipole orientation and space charge motion within the polymer.

2.8 ELECTROMETER :-

The "Electronics Corporation of India Limited" Varactor Bridge electrometer type EA 815 is high performance electrometer amplifier specially designed to measure very small direct currents, low DC potentials from high impedance sources, small charges and high resistances.

The extremely rapid response combined with its good stability and low drift characteristics, makes it a useful instrument in nuclear research, electrochemical and bioelectric measurements, spectrographic and electrophoretic studies, in measurement of grid currents of electrometer tubes and the contact potentials.

a) Specifications :-

Voltage Ranges : 10 mV, 30 mV, 100 mV, 300 mV, 1V, 3V & 10V of both polarities.

Input Impedance : $10^{14}$ ohms in the 'open' position of (Voltage measurement) the input resistance switch.
Current Ranges : $10^5$ to $10^{14}$ A. F.S.D. Both polarities in 28 overlapping ranges.

Input Resistances : $10^6$, $10^8$, $10^{10}$ and $10^{12}$ ohms selectable by a front panel Input Resistance selector switch.

Input Sensitivity : $10^{-16}$ A per division for current measurements.

0.1 mV per division for voltage measurement.

Accuracy of current : 3% in $10^6$, $10^8$ & $10^{10}$ ohms ranges 5% in $10^{12}$ ohms ranges.

Accuracy of Voltage : Built- in meter : 1% ± 0.1 mV on all ranges.

Measurements.

(at a Constant A.C Voltage)

Input Time Constant : 15 Seconds in $10^{12}$ ohms range. 10 seconds in $10^{10}$ ohms ranges reduces to insignificant time in other ranges.

Zero Stability : 0.3 mV/ 12 hrs.

Short Term Fluctuations: 0.1 mV r.m.s.

Effect of ±10% Mains : 0 ± 0.5 mV

(Voltage Variation).

Input Power : 210-250 V, A.C. 50 Hz.

b) Brief Circuit Description :-

The EA 815, Electrometer Amplifier is intended for the
measurement of DC potentials across high source resistances, very small direct currents, high resistances and very small charges. All the above measurements being carried out in terms of potentials.

The ranges covered by the instrument are 0-10 mV through to 0-10V of either polarity. The input resistance being greater than $10^{15}$ ohms and the zero drift of less than 0.3mV in 12 hours. The input terminal is specially selected for its high insulation characteristics.

The circuit comprises mainly of two parts, the Power Supply and the Varactor Bridge Electrometer.

1. The power supply provides $\pm 15$ and $-15$V regulated for the operation of the circuitry. Diodes D1 and D4 constitute a rectifier bridge across the 16-0-16V winding of the mains transformer with the centre tap as the reference. Capacitors C5 and C6 provide the filtering for the two lines. The two supplies are regulated using series type regulating circuits comprised of the series transistors Q1 and Q4, error amplifiers Q2 and Q3 and reference voltage zeners D5 and D6 respectively.

2. The Varactor Bridge Electrometer is an extremely low input bias current and high input impedance operational amplifier capable of high quality performance. In principle, the Varactor Bridge Amplifier design is similar to that of the vibrating read electrometer but with the inherent advantages of the solid state circuitry. It uses a hybrid integrated circuit chip (type 310 K- of Analog Devices) resulting in great compactness and reliability.
c) Operational controls :-

Input : Highly insulated teflon input connector receives input to be measured.

Input Resistance : Rotary switch selects input resistances as indicated the panel i.e. $10^6$, $10^8$, $10^{10}$ and $10^{12}$. In ‘OPEN’ positions, terminals will be available at the switch for connecting a capacitor of known value from the external circuit for charge measurements.

Mains : Switches ON the mains supply to the instrument when pressed. Glow of the pilot lamp indicates the presence of supply.

Zero Adjustment : 10 turn helical potentiometer to set the electrical ‘Zero’ of the meter.

Range : Rotary switch selects voltage ranges from 10V to 10 mV as indicated on the panel.

Polarity : Selects input polarity (+Ve or -Ve) and disconnects the meter from the circuit in OFF position.

Current-Voltage : Sets the unit for either current or voltage measurements.

Fuse : 100 mA
d). How to operate the unit-

Before switching ON the instrument make sure that the panel controls are as follows.

i. Current Voltage : in Current Position

ii. Range : in 10V position.

iii. Polarity : in 'OFF' position


v. Input socket closed with the metal dustcap provided.

vi. Input resistance in $10^6$ position.

e). Switching ON the unit -

i. Connect the instrument to the mains supply.

ii. Set the input resistance switch to $10^6$ ohms position and depress the mains switch. Presence of supply will be indicated by the glow of the pilotlamp.

iii. After a warm up time of about a minute set the polarity switch to the required polarity. Now the meter will indicate Zero. If that is not the case the instrument has to be suspected for some fault.

iv. If zero is obtained at 10V position then turn the range switch to the most sensitive range step by step and adjust the electrical zero of the instrument by turning the zero adjust potentiometer. This zero adjust potentiometer will be seen to have effective control only in the lower voltage ranges.

v. Adjustment of zero on the meter in the most sensitive range will hold good for any other range for a particular input resistance selected.
Since there may be slight variation in the contact potentials for different input resistances selected, a slight re-adjustment of the zero setting may be necessary in each case.

Hence to obtain accurate measurements within the capability of the instruments, it is essential to check and adjust meter zero prior to measurement every time the input resistor is changed. It is also essential to keep the range switch in 10V position before changing the input resistance switch setting.

vi. It is essential to allow for one hour warm up time for getting the best results while measuring very low currents charges and voltages.

vii. Now the instrument is ready for use.

f). **Current measurement** -

Current of the order of $10^{-5}$ A to $10^{-16}$ A can be measured by measuring the potential across the known resistance connected in the instrument.

i. Select the appropriate range by means of the range switch and the input resistance switch.

ii. Remove the dust cap and connect the current source by means of the antmicro phonic high impedance cable to the input socket.

iii. Select the desired polarity by means of the polarity switch and adjust the zero by means of the zero adjustment potentiometer.

iv. Apply the current and note the meter reading in millivolts or volts. Since the meter dial is calibrated in terms of voltage and input resistance is known by the switch setting, the current being
measured can easily be calculated from those two indications.

Temperature was measured with a precalibrated copper-constantan thermo couple. The thermoelectric e.m.f. generated was noted with a d.c. micro-voltimeter.

Capacitances and losses were measured with a LCR systronics bridge incorporating an audiofrequency oscillator (from Toshniwal).

Dry cells of 1.5V and dry batteries of 9V were used to apply the desired voltage to the film.

2.9 ELECTRICAL CONDUCTIVITY MEASUREMENT :-

Electrical conductivity of dielectrics is generally investigated either by heating the sample over a temperature range at a constant rate and keeping the applied voltage constant or by applying a voltage over a range keeping the temperature constant. Both the procedures have been adopted in the present investigation on electrical conduction.

Current voltage characteristics at different temperatures were traced by applying a voltage in the range 1.5 -90V. When the film equilibrated at a particular temperature, a voltage was applied. The current was found to decrease first rapidly and then slowly to reach the steady value. The voltage was varied in steps of 1.5V upto 9V and then in steps of 9V upto 90V.

Current temperature curves of various films were obtained by heating the sample at a rate of 1°C min⁻¹. A voltage of 90V was applied to the film. The currents were noted at regular intervals of temperature.
2.10 THERMALLY STIMULATED DISCHARGE CURRENT MEASUREMENT :-

When the film equalibrated at a desired temperature, an electric field was applied for 30 minutes and was cooled with the field still applied to about 20°C. The thermoelectret, thus formed, was short circuited for 2 minutes to minimize the stray surface charges. The electrets were heated at a linear heating rate of 3°C min⁻¹ to observe the thermally stimulated discharge current (TSDC).

2.11 PHOTO DEPOLARISATION CURRENT MEASUREMENT :-

Photoelectrets were fabricated by applying an electric field for desired time in the presence of UV illumination. The electrets, so formed were preserved in dark for 1 minute to reduce stray surface charges and were depolarized by the same radiation.

2.12 CAPACITANCE AND LOSS FACTOR MEASUREMENT :-

Dielectric properties of pyrene doped PS were investigated by measuring simultaneously the capacitance and the loss factor over a wide range of frequencies and temperatures. When the film equilibrated at a desired temperature, the capacitance and the loss factor were measured by varying the frequency in audio frequency range.