CHAPTER II

EXPERIMENTAL TECHNIQUES
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Introduction:

Miniaturization of solid state devices used in electronic instruments has provided a new family of investigation which is interesting as well as promising. Organic insulating materials in thin films form are being extensively studied. Polymers with their high insulating properties may play an important role in the fabrication of such devices. Different types of studies have been observed by several workers with many interesting results. Generally the different phases of crystalline and amorphous phases are extended in to each other and thus the dielectric properties may very much depend on the mechanical and thermal history of polymer. The properties of a large variety of new and exotic materials obtained by thin film technique will undoubtedly draw considerable attention in the future.

The details about various techniques of film formation isothermal immersion growth technique, alongwith the experimental technique used in present investigation types of electrodes vacuum coating unit to deposite the electrodes and electrode geometry are discussed in this chapter.
2.2: Methods of Sample Preparation:

Over the past few years methods of depositing thin films have been reviewed in numerous texts\textsuperscript{1-4} as far as physical and chemical techniques are concerned.\textsuperscript{1-3} The specific application of growth methods to dielectrics has also been recently reviewed,\textsuperscript{4} and more recently still, the review of methods of deposition has been updated in terms of the deposition systems which have become of interest over the last few years.

A summary of techniques that can be used for preparing dielectric thin films is given in table 2.1. The distinction between physical and chemical techniques is shown; physical techniques being those which depend on the physical evaporation or ejection of materials from the source, whilst, chemical techniques depend on a reaction such as the electrical separation of ions, as in electroplating and anodization or thermal effects on chemical reactions, as in vapour phase deposition and thermal growth. There is considerable overlap between two basic methods, because some physical systems of deposition also involve chemical reaction as in the case of plasma reactions shown under sputtering.
Table 2.1: Summary of preparation methods applicable to dielectric films.

<table>
<thead>
<tr>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation (using all source types)</td>
</tr>
<tr>
<td>Reactive, Sputtering - Reactive.</td>
</tr>
<tr>
<td><strong>Physical:</strong></td>
</tr>
<tr>
<td>rF</td>
</tr>
<tr>
<td>Ion implantation.</td>
</tr>
<tr>
<td>Plasma reactions.</td>
</tr>
<tr>
<td>Gaseous anodization.</td>
</tr>
<tr>
<td>Assisted thermal growth.</td>
</tr>
<tr>
<td>Polymerization.</td>
</tr>
<tr>
<td>Assisted vapour - phase.</td>
</tr>
<tr>
<td><strong>Chemical:</strong></td>
</tr>
<tr>
<td>Oxidation</td>
</tr>
<tr>
<td>Nitriding</td>
</tr>
<tr>
<td>Solution deposition oxides from colloids and solutions,</td>
</tr>
<tr>
<td>Langmuir,</td>
</tr>
<tr>
<td>Polymer.</td>
</tr>
<tr>
<td>Casting</td>
</tr>
</tbody>
</table>
The techniques shown in Table 2.1 are all capable of producing films, (1-20 μm), thick. Other techniques are available for producing only thick films, such as glazing, electro-phoretic deposition, flame spraying, painting and screen printing. These techniques have been summarized in "Science and Technology of Surface Coating".6 and sections dealing with the screen printing of dielectric layers in the "Handbook of Thick Film Hybrid Microelectronics".7

Particularly, polymer films can be obtained by exposing the monomer vapour at a reduced pressure to electron beam,8-10 glow discharge11,12 or ultraviolet radiations.13,14 Recently, laser beam evaporation15 and RF sputtering16,17 have been found to be useful for the preparation of polymer films but the easiest and preferential immersion technique.18,19

The film formed by all other methods except the "isothermal immersion technique" are either branched or cross linked20 and contain a large number of pinholes which causes discontinuity in this film. The films so formed show high dielectric losses while cross linking promotes degradation. These films are, therefore, not suitable for practical applications.
On the other hand, structurally reproducible, coherent, uniform, smooth films free from pinholes can be grown from solution by isothermal immersion method. The films have been obtained by the simple technique of direct isothermal deposition of suitable solution on to a substrate. The evaporation of solvent (viz. benzene results in transparent layer of PS. The chances of crosslinking of the polymer chains are very low. Thus, these films are not only simple and reproducible but are most reliable and hence useful for practical applications.

Epitaxial growth,\textsuperscript{21-23} X-ray diffraction studies,\textsuperscript{24} nature\textsuperscript{22,23} and other properties of films with deposition techniques have been dealt with at length recently in a number of reviews\textsuperscript{5,25,26} and books.\textsuperscript{27,28}

2.3: Isothermal Immersion Technique:

It is obvious from the above that the best quality smooth films free from pinholes can be grown by this method. The description of the apparatus has been reported in detail by Rastogi.\textsuperscript{29} They found out that the rate of growth of film and the ultimate film thickness depend on the nature of substrate, concentration and the temperature of the solution and the time for which the substrate is kept immersed in solution. When the solution and the
FIG. 2.1 - A DIAGRAM OF THE ISOTHERMAL IMMERSION TECHNIQUE FOR GROWING THE THIN FILMS.
substrate attain the required temperature, the substrate is slowly moved down by a suitable arrangement for a period ranging from 5 minutes to 30 minutes (for different thicknesses of the film) and after the withdrawal from the solution the substrate with deposited films are washed in solvent and dried in hot air. Solution technique is more suitable method when doping of the polymer matrix is to be tackled. In practice, it is necessary to take care of the following.

2.3-1: Choice of Substrate and its Cleaning:

A good substrate should not react with polymer, its solvent and its surrounding atmosphere. It should be resistant to chemical corrosion, especially to those materials which are commonly used for cleaning purpose. Its softening and melting points should lie much higher than the temperature of investigation. It should be made of hydrophobic material.

There are various substrates such as mica, molybdenite, rock salt, metal foil, glass, however, glass is the best of all. For technological purposes glass substrates are frequently used so that the adsorption and surface diffusion energies on the smooth surface are fixed for the material being deposited. In general, the
adsorption energy is smaller on glass than on any other substrates.

Optically plane glass plates made of high quality glass were used in the present investigation and also in other reported works. They are cheap and ready for repeated use after proper cleaning. Metal foils have an inherent disadvantage that they usually react with the ambient oxygen to form an oxide layer over the surfaces. Similarly crystals like NaCl are more or less hygroscopic and their surfaces are easily contaminated.

Cleaning of glass plates in the present investigation was done first by washing in tap water with some detergent. After drying these glass plates, they were then washed with benzene, so as to remove the contamination left behind.

2.3-2 : Effect of Solvent :

The transition of polymer solution into solid polymer has been examined in numerous investigations and several aspects, e.g., phase equilibrium in polymer solvent system separation of the polymer into phases and growth of nuclei, metastable solutions and spontaneous ordering of the problem can be distinguished. Tager and his collaborators have
reported that a good solvent increases the flexibility of polymer chains, which favours production of denser films.

To grow the best quality, optically smooth films free from pinholes, the rate of vaporization of the solvent should be kept sufficiently slow. This can be achieved by using a solvent of high boiling point. In the present case Chloroform was used throughout this work. Further, slow vaporization can also be achieved by allowing the films to dry up in the atmosphere of solvent itself.

2.3-3: Solution Concentration:

It is preferable to use the solution of low concentration for the film deposition. Experiments indicate that the film grown from thick solutions have considerably different thicknesses at different special points. They may also entrap air bubbles in their structure.

The effect of concentration on the preparation of films has been reported\textsuperscript{40} and reviewed by Kargin.\textsuperscript{41}

2.3-4: Solution Temperature:

Solution temperature markedly affects the growth of
the films. Hot solution give rise to thinner depositions due to lower value of viscosity. It is better to use a solution whose temperature lies in the neighbourhood of room temperature. It is necessary since the substrate acquires the temperature of the solution when the later is poured into it and if it is much higher than room temperature, the rate of vaporization of solvent would greatly enhance during the process of drying, which is undesirable. The temperature of the solution was kept a bit higher (about 5°C) than room temperature so as to make the compensation for temperature fluctuations arising due to change in weather.

2.4: Preparation of Films:

Samples used in the various investigations were solution cast films. Commercially available polymethyl methacrylate (PMMA) granules have been used in the present study. Chloroform solution of polymer composite (concentration 2.1 gms PMMA in 30 cc. chloroform and different weight ratios of Ferrocene/Malachite Green were taken) was poured on to clean glass substrate. The evaporation of chloroform resulted in transparent layer of composite of about 20 μm thickness. After solvent evaporation, the films were dried for 24 h. Since the adhesion of layers to the glass substrate is poor, the layers could be easily detached from it.
2.5: Thickness Measurement:

Thickness of the polymer films can be measured through a variety of methods. They may be divided into three categories.

2.5-1: Mechanical:

It includes two important methods, namely stylus\textsuperscript{42,43} and weighing\textsuperscript{44,45} methods. In spite of their simplicity, their accuracy is very low (reported ± 25%).

Stylus method consists of a fine pointed stylus whose mechanical motions along the thickness of the film are used to compute its thickness. The stylus is moved over a stepped surface formed by the edge of the film and the substrate. The transverse vibrations suffered at the step are fed to an electronic circuit for amplification and recording.

The second mechanical method of film thickness measurement consists in weighing a well defined area of the substrate before and after deposition of the film. The thickness $t$ of the specimen is given by:

$$t = \frac{w}{sd}$$

where $w$ is the weight of the film, $s$ its surface area and
\( d \) is the density of the material. Obviously, the sensitivity of the method depends upon the measuring accuracy of \( a \) and \( w \). But its main defect is that it is not always possible to cut the substrate in a well defined area. Further, the area selected for thickness measurement may not be representative of the area under investigation.

2.5-2: Optical:

Out of various methods falling under this category, following three are of importance. They are ellipsometry\(^{1-3,46}\) light cross section method\(^{47,48}\) and interferrometeric method.\(^{49}\)

Ellipsometry is a nondestructive method for measuring the thickness of transparent films. It is based on evaluating the charge in the state of polarization of light reflected from film and substrate. The method, no doubt, an accurate one, involves long, time consuming, complicated mathematical calculations of complex nature. Hence it is not in common use.

Light-cross-section method involves simple optical device which allows the measurement of both transparent and non-transparent films in the 1 to 50 \( \mu m \) interval by the contactless method. In this method a narrow illuminated
slit is projected by a microscope onto the stepped surface formed by the edge of the film and the substrate at an angle of 45° with respect to the film surface. Two images of the slit are observed, one after reflection from the substrate and the other from the upper surface of the film. Reported accuracy is ± 5%. But the main difficulty of this method is that it requires optically plane films.

Interferometric methods include those devices which make use of interference of light; Newton's rings, Michelson's interferometer, Fabry-Parrot etalon are such devices. The method is based upon observing the shift of interference fringes on moving from film surface to the substrate. But optical smoothness of the film surface is again a prerequisite.

2.5-3: Electrical:

Measurement of capacitance is a simple, effective and non-destructive method of film thickness measurement. The method may be used for both opaque and transparent film with the same accuracy. Its specific advantage lies in the fact that one gets the thickness of that particular area, which is actually involved in an investigation. The method consists in measuring the capacitance of the sample
by a sensitive L-C-R bridge, making necessary compensation for the capacitance of leads, assembly etc. Let $C$ be the capacity of a sample, its thickness can be calculated from the relation.

$$t = \frac{8.854 \times 10^{-12} S}{C}$$

where $S$ is common geometrical area of the electrodes on both sides of the film. $C$ is the capacity in Farad and $\varepsilon$ is the high frequency dielectric constant of the film material, which can be read from tables.

The method is in extensive use now a days. Its only disadvantage is that it requires pre-knowledge of $\varepsilon$ which may not be possible in typical cases. As polystyrene is well known for its constant $\varepsilon$ value, the method was the best suited and thereby it has been used to compute the film thickness in the present case.

2.6: Electrode Effect:

Contacts play an important role in all electrical measurements made with the insulator. The concept of polymer work function $\Phi$ gained acceptance after the work of Davies and is important for discussing all aspects of polymer contact phenomena.
Contact materials and configurations used in electrical measurements vary widely and depend on the particular application. Metal electrode can be attached to the samples by evaporation, ultrasonic soldering (e.g. indium or indium-gallium alloys and gold), by application of conductive paste (silver paint or epoxy) or metallographic compounds (noble metals precipitate upon heating the sample and organic residue evaporates).

Electrical properties of polymer films are usually studied with various electrodes namely (i) Pressed Metal-Foil electrodes (ii) Painted Electrodes (iii) Vacuum-deposited Electrodes.

For investigating intrinsic relaxation properties, the electrode dielectric contact should be practically "invisible". This is practically not possible. The problem of applying electrodes and their adhesion to sample, therefore, plays a key role in the determination of electrical properties of solids. This is particularly true in current TSD and electrical conductivity measurements, where generally large changes in temperature are involved. Poor contact will lead to irreproducible measurements, high noise level, poor agreement between results from different samples of same material and some-times
additional current peaks due, in particular, to homocharge function. As reported in literature\textsuperscript{56} the most convenient way to avoid these difficulties is to use metal films carefully evaporated on to cleaned surfaces, without this cleaning procedure parasitic currents may be observed in certain materials.\textsuperscript{57} But on account of some practical difficulties, this method could not be employed for the present study.

Results may change due to the effects, which may when other types of electrodes were used. To remove these defects vacuum coated electrodes are to be used. The deposition of electrodes was done by vacuum coating unit.

Vacuum Coating Unit:

Vacuum coating was done by evaporating desired metal by heating it to sufficiently high temperature under vacuum and condensing the vapour on to the cooler substrate/film. Evaporation in vacuum (lower than $10^{-5}$ Torr) is necessary as otherwise the vapour molecules are deflected from their linear path owing to collision with the ambient air molecules.

Operation of Vacuum Coating Unit:

The main parts of vacuum coating unit are shown in
sketch diagram (fig. 2.2). The different parts, are rotary pump, diffusion pump, transformer for L.T. and H.T., coating jar.

To start with all the valves, i.e. high vacuum valve, backing and roughing valves are closed and the rotary pump starts evacuating the tube connecting the rotary pump and the junction of the backing and roughing valves. The pressure can be read on a Pirani Gauge fitted near the junction. When this pressure falls below 0.05 torr, backing valve is opened so that the diffusion pump is connected to the rotary pump and starts getting evacuated. At sufficient low pressure the diffusion pump is started with water circulation and the heater is also in ready position before this use.

After lifting the bell jar (air inlet valve in open condition), the metal foil or powder is kept inside the tungsten filament or boat and cleaned substrates with proper mask are kept on substrate holder directly above the filament (or boat). The bell jar is replaced on the base plate with gasket, and air admittance valve is closed. Now the backing valve is closed and roughing valve is opened so that the rotary pump is directly connected to the vacuum chamber. The rotary pump now starts evacuating with the vacuum chamber. At pressure
FIG. 2.2- BLOCK DIAGRAM OF VACUUM COATING UNIT.
about 0.8 torr in the chamber a high tension is applied to H.T. electrodes for only 2 minutes. At this time, the chamber is filled with a violet glow due to ionization of air and the substrates get cleaned by ionic bombardment. At sufficient low pressure (or vacuum 0.01 torr), the roughing valve is closed and backing valve open, the high vacuum or baffle valve is opened so that the vacuum chamber is connected to diffusion pump. With in about one hour, ultra high vacuum is produced in the chamber when the pressure inside the chamber becomes $10^{-5}$ torr or even less than this, the L.T. supply connected to L.T. electrodes and at first small magnitudes of current is passed from filament or boat for degasing of the metal foils and sometimes the L.T. current may be off if necessary.

When a pressure attains a steady value of $1 \times 10^{-5}$ torr, the current in the filament or boat first melts the foils and then evaporated and gets deposited on the substrates kept above the evaporation source.

The current through the filament and diffusion pump, heater are switched off. The penning gauge is switched off and baffle valve is closed immediately after the deposition of electrode material. After 10 minutes of
these processes the bell jar may be removed to take out the cooled slides.

We have used vacuum coated electrodes throughout the present investigation. As glass possesses almost all desired properties of a good substrate, it was chosen for sample preparation in most of the studies in the present work. For sandwich structure (M₁ - composite film - M₁/M₂) in thin films, the lower electrode was deposited on the clean glass slide and then it was suspended vertically for 10 minutes in the glass beaker containing polymer solution of desired concentration and polymer film was grown on 3/4 portion of it, leaving 1/9th portion of lower electrode. After the film deposition, the glass slide was taken out and dried. After the film was dried, Al/Ag/Cu was vacuum deposited over the upper surface of the film with the help of an aluminium mask in such a way that a circular portion of area 1.33 cm² overlaps the lower electrode and its tail extends to the other end of the slide for electrical connections, thus, a sample in the sandwich structure of M₁-polymer composite-M₁/M₂ was obtained with pressureless contacts (fig. 2.3). Samples of different thicknesses were obtained by changing the concentration of the polymer solution.
FIG: 2.3 - CIRCUIT DIAGRAM FOR MEASUREMENT OF CURRENT IN ELECTRODE-SANDWICH CONFIGURATION.
2.7: Instruments Used and Their Specifications:

A small size thermostat (1 x 1 x 1 ft$^3$) was designed and fabricated in Workshop Deptt. of Physics, University of Sagar, for heating the sample at a sufficiently high rate (2 - 4°C/min.). Temperature of this thermobox could be controlled by a variac. For the study of electrical conductivity, which requires a constant temperature for a long time, this thermostat could be used. Temperature was measured with an accurate mercury thermometer.

The sample holder used for experimental work was also fabricated in the university workshop. The section diagram of sample holder is shown in fig. 2.4. It consists of a brass plate 10 x 6 cm. in size and 4 mm thick. Above the brass base plate, a mica sheet of 1 mm thickness is placed. The glass slide with composite film with vacuum deposited electrodes is placed on the mica sheet so that it remains insulated from the brass plate. To make electrical contact with vacuum deposited electrodes, two brass cylinders are placed over them as shown in the figure (2.4). The brass cylinders are held in their positions with the help of fly screws fitted to the horizontal arm of two bridges fitted to the base plate.
DIAGRAM OF DOUBLE BRIDGE ELECTRODE ASSEMBLY.

FIG: 2.4
The cylinders are insulated from fly screws and brass bridges using teflon disc. Connecting leads are soldered to the brass cylinders for making connections with power supply source or the electrometer amplifier.

Current Measuring Instrument:

The currents were measured with a Keithley 600B electrometer which was carefully shielded and grounded so as to avoid ground loops or extraneous electrical noise. It is important to make use of high insulation amphenol cable supplied along with the electrometer in order to connect the sample directly to the electrometer.
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