2. EXPERIMENTAL TECHNIQUES

2.1. INTRODUCTION

A number of polymers of long chain and high molecular weight have very complex and considerable variety of physical and chemical structures. Also most of the polymers are having a mixture of polycrystalline and amorphous regions. The ratio of this mixture depends strongly on the method of preparation and the impurities incorporated. Thus, it has not been possible to obtain reproducible and unambiguous results on polymer films obtained by vacuum evaporation [1], glow discharge [2] and electron-beam irradiation in vacuum [3]. However, uniform, structurally reproducible and pinhole-free films with minimum ageing effects can be produced by the solution growth technique [4-5]. This chapter deals with the experimental details of the preparation of PI and iodine doped PI films. The experimental methods employed in the present investigation for the study of structural, dielectric, conduction, TSDC, breakdown, and laser damage properties of the polymer films have been discussed in the relevant chapters.

2.2. SOLUTION GROWTH TECHNIQUE

The technique used for deposition of thin films in the present study was solution growth technique which involves the isothermal immersion of the substrate into the polymer solution of suitable concentration held at a constant temperature for a certain time. The rate of growth and the thickness of the film depend on the nature of the substrate, the concentration, and temperature of the solution and on the time for which the substrate is left immersed in the solution. The experimental arrangement for solution growth technique is shown in Fig.2.1. Polyimide (PI) films were deposited from a polyimide solution. The polyimide solution was prepared by dissolving 2.5 gm. of PI in 20 cc of ethyl acetate. The solution was continuously stirred by means of a magnetic stirrer to ensure a homogeneous mixing. In the same way 0.8% and 2% iodine doped PI films were
Fig 2.1 Solution growth technique.
prepared from 0.8 and 2% iodine concentrated homogeneous solution of 2.5 g PI dissolved in 20 cc of ethyl acetate. Films were grown on predeposited aluminium electrodes on a glass substrate. The substrates with film were withdrawn from the solution and dried in a hot air oven for 8 hours at a constant temperature of 423 K.

2.3. VACUUM COATING UNIT

Fig 2.2 shows the schematic diagram of the conventional vacuum coating unit. In the present study, a 12 A4 type (Hind Hivac, Bangalore, India) coating unit was used for the deposition of electrodes. The three main parts of the unit are (i) the vacuum chamber (ii) the pumping or the evacuating system and (iii) the electrical equipment with connections. The vacuum chamber is evacuated by a 4" oil diffusion pump which is in turn backed by a double stage rotary pump which has an evacuating capacity of 200 litres per minute. A magnetic isolation cum air admittance valve in the system serves as a safety accessory. DC 704 silicone fluid, that has a low vapour pressure of \(1.33 \times 10^{-5}\) Pa, is used as the diffusion pump fluid. A Pirani gauge, that works on the basis of thermal conductivity, is used for measuring the chamber pressure at low vacuum (66.5 to 1.33x10\(^{-1}\) Pa). For the measurement of very low pressures (1.33x10\(^{-1}\) to 1.33x10\(^{-4}\) Pa), a Penning gauge is employed. The resistively heated source is energised by an L.T. transformer having a high current supply.

2.4. THICKNESS MEASUREMENT

The commonly used thickness measurement methods are (i) mechanical method (ii) ionization method (iii) microbalance method (iv) radiation method (v) optical method and (vi) capacitance method [6-12]. The optical method that employs the interference technique has been found to be the most suitable method for the measurement of film thicknesses of the
1. ROTARY PUMP
2. MAGNETIC ISOLATION VALVE
3. BUTTERFLY VALVE
4. PIRANI GAUGE I
5. PIRANI GAUGE II
6. PENNING GAUGE
7. BACKING LINE
8. GLASS OR METAL BELL JAR
9. DIFFUSION PUMP
10. DIFFUSION PUMP HEATER
11. LIQUID AIR TRAP
12. AIR ADMITTANCE VALVE
13. NEEDLE VALVE
14. BAFFLE VALVE

FIG. 2.2 SCHEMATIC REPRESENTATION OF VACUUM COATING UNIT
order of the wavelength of light. The thicknesses of the electrode films used in this study have been measured using this optical (multiple beam interferometer) method. Since the thicknesses of the polymer films in the present study are very high, other methods of thickness measurements like, mechanical, capacitance and microbalance methods have been used. In the capacitance method, which has been widely used for the polymer film thickness measurements [13-16], the thickness of the polymer film is estimated from the measured value of the capacitance of the metal-polymer-metal (MPM) sandwich structure. The formula used to calculate the thickness is,

\[ C = \varepsilon' \varepsilon_0 A/d \]  

where \( \varepsilon' \) is the dielectric constant of the polymer, \( \varepsilon_0 \) is the permittivity of free space (\( 8.854 \times 10^{-12} \text{ Fm}^{-1} \)), \( d \) is the thickness of the film and \( A \) is the area of the electrode. The value of dielectric constant for PI used in the present study is 3.2 [17]. The thicknesses of the polymer films were also determined by mechanical method, using stylus. The thickness values obtained from the two methods were found to be in good agreement with each other.

2.5. SAMPLE PREPARATION

2.5.1. Substrates

The substrates serve as a mechanical support for the film and in electronic applications, it also serves as an insulator. The need for long term stability makes it imperative that no chemical reactions occur which would change the properties of the film. The substrates should have mechanical strength and there must be a good adhesion between the film and the substrate at room temperature as well as at very high temperature. The substrate should also have an appropriate heat conductivity to ensure constant temperature of
the surface and sufficient heat removal during the operation of electronic
devices. The surface of the substrates should be flat and smooth to form the
films with well defined and reproducible electrical and other parameters.

A number of materials like glasses, ceramics, quartz are available for use
as thin film substrates. Of all these materials, glass has the maximum surface
smoothness and is also optically plane[18]. It is easily and cheaply available
and has a low cost. Hence in the present study, glass microslides have been
employed as the substrates. Table 2.1 presents the sizes of the glass
microslides used for different studies.

Table 2.1. Sizes of glass substrates used for the different studies.

<table>
<thead>
<tr>
<th>Study</th>
<th>Substrate size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>1 cm. x 1cm.</td>
</tr>
<tr>
<td>Dielectric, conduction, TSDC and Breakdown</td>
<td>3.75 cm. x 2.5 cm</td>
</tr>
<tr>
<td>Laser damage</td>
<td>7.5 cm. x 2.5 cm.</td>
</tr>
</tbody>
</table>

2.5.2 Substrate cleaning

The cleanliness of the substrate exerts a decisive influence on film growth
and adhesion and hence is essential for the preparation of films with
reproducible properties. The following procedure was employed for cleaning the
glass substrates. Initially the micro slides were immersed in a soap solution
and distilled water. Next they were subjected to ultrasonic agitation. The shock
waves remove the residues from the substrates. The films were then subjected to vapour degreasing using isopropyl alcohol. This increases the rate of dissolution of surface contaminants. Finally the substrates were kept in an oven for drying.

2.5.3 Masks

Masks prepared by photolithographic method [19] have been employed to form the desired patterns of thin film samples. Brass masks were employed for electrode (Aluminium) deposition. The masks should be cleaned prior to evaporation to remove surface contaminants that might become volatile when heated. These contaminants might be absorbed by the substrates and cause a weak spot in the film coated on it. The masks were initially cleaned with acetone and then heated for about half an hour at 150°C. They were then ultrasonically agitated and finally dried in an oven.

2.5.4 MPM Structure

Metal-Polymer-Metal (MPM) sandwich structures were formed onto glass substrates with the insulating layer in between the two metal electrodes by making use of suitable masks as shown in fig 2.3. The fabricated MPM structure and its vertical cross sectional view are shown in fig. 2.4. The electrode material should be such that it does not react with the dielectric film and should have good adhesion with the substrate and also a low electrical resistance. Metals like gold, silver, copper and aluminium are used as electrode materials. Of these, aluminium has been observed to possess all the desirable properties while the other materials are found to be lacking in one or the other. Hence aluminium has been used as the electrode material in the present study.
Fig. 2. 3. Masks used to form MPM structure.
Fig. 2 MPM sandwich structure and its vertical cross sectional view

1. Substrate
2. Bottom electrode
3. Dielectric Polymer film
4. Top electrode

Electrode Overlapping Area (A)
The conventional vacuum coating unit described in section 2.3 was employed for the deposition of the electrodes. Pure aluminium (99.99% Balzers) was evaporated at a pressure of $1.33 \times 10^{-3}$ Pa from a helical tungsten filament, by resistive heating onto well-cleaned glass substrates through suitable masks to form the base electrode. The source to substrate distance was maintained at 0.18m. Prior to evaporation the aluminium was degassed under the shutter for two minutes. After evaporating aluminium to form the base electrode, the dielectric material was deposited by solution growth (details are given in section 2.2). Finally the top electrode was formed by again evaporating aluminium, thus completing the MPM structure.
References