CHAPTER III

MATERIALS AND METHODS
This chapter deals with the selection of materials, various methods of polymer film-preparation, experimental techniques employed in the present investigation, the measurement of thickness, substrate cleaning, measurement of electrical conduction, Thermally Stimulated Discharge Currents, Pyroelectric current and Dielectric Properties.

3.1. Selection of Materials

Cellulose acetate-butyrate (17% butyryl content) used in the present investigations was obtained from Lobo Chemicals India Limited, Bombay. The structure of the cellulose acetate-butyrate (CAB) is:

The above structure shows the partial polar nature of CAB polymer. Its polar nature is due to the electronegativity difference between "C" and "O" molecules of C-O-C bond in its main chain and -O-C-CH₃ (acetylate) and -O-C-C₂H₇ (butyrylate) and -O-H (Hydroxyl) groups present in the side chains.
The data collected from literature for CAB polymer material from the point of view of electrical properties are given below.

Glass transition temperature \( T_g \) = 323 K.

The range of dielectric constant \( \varepsilon' \) at frequency \( 10^6 \) Hz and Temperature 25°C = 3.2 to 6.2

The range of dissipation factor \( \varepsilon'' \) at frequency \( 10^6 \) Hz and temperature 25°C = 0.02 to 0.05

The range of dielectric strength = 250 to 400 V/Mil

The volume resistivity \( \rho \) = \( 4 \times 10^{13} \) ohm-m

It is clear from the above data that the CAB polymer is a good dielectric and it is also a promising electret material, as the CAB polymer has polar groups.

CAB has a wide variety of applications in film products because of their excellent dimensional stability and lower water absorption as compared with the other cellulose materials.

Hence CAB is chosen in the present study for investigation of electric and dielectric properties like electrical conduction, thermally stimulated depolarization currents, pyroelectric behaviour and dielectric properties. For the study of dopant effect on CAB, iodine is chosen being a good acceptor material.

In the present studies pure aluminium (99.9%) was chosen for the electrode material. Pure silver (99.9%) was also used to study the electrode effect on CAB films.
3.2. Methods of Polymer Film Preparation

A number of methods are available for the formation of polymer thin films. Some excellent reviews appeared in the literature on the polymeric film preparation. Some of the important methods are outlined below.

3.2.1. Spray Coating

Most spray methods are based on the principle of atomizing the point into a fine mist, which is then directed to the surface to be coated. Atomization is accomplished by the use of compressed air, pressurized volatile solvents or a high-velocity jet stream. For the deposition efficiency, the electrostatic spray process is used. These spray processes are used for coating the polymeric material to the electrical parts.

3.2.2. Dip Coating

As the name implies, dip coating is the immersion of a part into a liquid composition, withdrawal and drying. It is a highly desirable method for achieving pinhole free and continuous films with uniform thickness. The rate of growth and thickness of the film depend on the viscosity of the bath, the rate of immersion and withdrawal and the temperature of the bath. Many polymer films have been prepared by this technique.

3.2.3. Vacuum or Vapour Deposition

The vacuum or vapour deposition of coatings, though a highly desirable method, can be employed for only a few polymer types. Unlike
metals, most polymers cannot be heated to their vaporization temperatures without gross decomposition and changes in their physical and electrical properties. The polymers like polyethylene and Teflon can be deposited using this process.

3.2.4. Laser Evaporation

In this method, the material is heated by the enormous power of a laser source. The evaporation generally takes place from the surface of the material only. Very thin films can be obtained as the amount of energy released in each burst is very large. Crystalline polymers evaporated by this retain their original structure with excellent electrical properties

3.2.5. Ultra-Violet Light Polymerization

Gaseous monomers absorbed onto a surface may be polymerized by exposure to ultraviolet light. The deposition chamber is normally evacuated to about $10^{-6}$ torr to remove water vapour and the gaseous monomer is introduced and maintained at about 4 torr during irradiation. Monomers most suitable for ultraviolet polymerization are those containing double bonds like styrene butadiene, methylmethacrylate etc.

3.2.6. Plasma Polymerization

In this technique polymer thin films are obtained by creating a plasma in the evacuated chamber and polymerizing the corresponding monomer. A pair of electrodes in a glass belljar is separated by a gap of 40 $\mu$m for AC plasma and 20 $\mu$m for the RF plasma. This method is very useful for the preparation of semiconducting polymer films.
3.2.7. Langmuir - Blodgett Technique

Langmuir-Blodgett films are prepared by depositing a small quantity of a solution of a suitable material onto a liquid surface, waiting for the solvent to evaporate and then compressing the monomolecular layer so produced until it forms a quasi-solid one molecule thick. In order to remove monolayers from the subphase a suitable substrate is dipped and raised through the compact monolayer. Various organic materials have been deposited by this technique.

3.3 Present Experimental Technique

The present technique for deposition of polymer films was solution growth (dip coating) technique, which involves the isothermal immersion of the substrate into the polymer solution of suitable concentration, constant temperature and dip time.

Cellulose acetate butyrate (CAB) films were deposited from the solution of fixed concentration of 2.5 gm of CAB dissolved in 100 ml of the ethylacetate (solvent). The solution was continuously stirred by a magnetic stirrer for about two hours to ensure homogeneous mixing. The solution was maintained at a constant temperature.

The CAB films were grown on predeposited aluminium electrodes on the flawless glass substrates. The filmed substrates were withdrawn from the solution and dried in a hot air oven for 24 hours at a constant temperature of 85°C to eliminate the solvent. Two counter electrodes also of aluminium were then deposited on the well dried CAB films to form the required Al-CAB-Al sandwich configuration. For the doped films
different concentrations (wt%) of iodine was added to the polymer solution.

3.3.1 Vacuum Coating System

The metal electrodes were deposited by Vacuum evaporation technique using a Vacuum Coating unit assembled in the laboratory (Fig. 3.1). A Vacuum of $2 \times 10^{-6}$ torr was achieved in the evaporation chamber. Pirani-Penning gauge systems were used to measure the Vacuum in the evaporation chamber. The material is evaporated using resistive heating of a tungsten spiral boat. Metal electrodes of aluminium and silver were formed using high purity (99.99%) starting material.

3.3.2 Masks

Different masks were prepared from aluminium sheet for obtaining film patterns that were necessary for various studies. The designs of several masks used in the present investigations are shown in Fig. 3.2. In the figure (a) and (c) are masks used for depositing thick electrodes for electrical measurements. The mask of Fig. (a) is employed to deposit bottom electrode and Fig. (c) is used to deposit top electrode Fig. (b) shows the polymer film. Fig. (d) represents the final form of the Metal-polymer-Metal sandwich configuration. The shaded portion represents the effective area of the sandwiched film.

3.3.3 Substrate Materials and Cleaning

The quality of the surface is the most important property of the substrate, the nature of the substrate has a significant influence on the growth of the film and this, in turn, has a profound effect on the
FIG. 3.1 PHOTOGRAPH OF VACUUM COATING SYSTEM
Fig. 3.2 Different metal masks employed for the preparation of MPM Structure: (a) bottom electrode, (b) polymer film, (c) top electrode and (d) complete MPM Structure.
properties of the film. The preparation of the film with reproducible properties would necessitate the substrate surfaces to be chemically inert and thermally stable. Hence, inorder to obtain uniform films with good adhesion and stability, well cleaned smooth surfaces are essential.

In the present investigation, microglass slides of "Blue star" were used as substrate material. They were well cleaned using the following procedure. First the glass substrates were immersed in hot chromic acid for two or three hours and washed in running tap water. Inorder to remove greasy or oily contaminants the substrates were scrubbed vigorously with "gentle" a liquid cleaner and a detergent. The substrates were rinsed in tap water and in double distilled water and finally rinsed with acetone. Then the cleaned substrates were dried in a hot air oven.

3.3.4 Measurement of Film Thickness

A number of methods are available for the measurement of thickness of a thin film. Among them a few methods like mechanical stylus method, gravimetric method, capacitance method are suitable for the measurement of thickness of the polymer thin films.

In the present investigation the thickness of the films was measured by mechanical stylus method by forming a step on the substrate and verified by gravimetric method and capacitance method.

3.3.5 Electrical Conduction

The experimental set up used for the study of electrical conduction is shown in Fig.3.3 and the block diagram representing the
FIG. 3.3 PHOTOGRAPH OF EXPERIMENTAL SET UP FOR THE CURRENT MEASUREMENTS
various connection is shown in Fig.3.4. The experimental CAB film was mounted in an experimental jig which was placed in a brass vessel evacuated to a pressure of 10^-3 torr (Fig.3.5). All the connections were perfectly insulated using teflon amphenols. The films were annealed by keeping them at a temperature of 400 K for about two hours.

The films, thus annealed, were used for electrical conduction measurements i.e., electrical conductivity and I-V characteristics. By varying the temperature, the corresponding current passing through the film was measured by an electrometer amplifier (Keithly 617 C), with an accuracy of ±10^-15 A. The temperature was monitored by a copper-constantan thermocouple kept in the close vicinity of the experimental film. The electrical conductivity and current-voltage characteristics were studied in the temperature range 300-450 K and the applied voltage range 0-300 V.

3.3.6 Thermally Stimulated Depolarization Currents.

The thermally stimulated depolarization currents (TSDC) were studied on sandwiched CAB films. The experimental arrangement is the same as that shown in Fig.3.3. To study the TSDC, the well annealed films were poled at a desired temperature, and different polarizing field strengths for a fixed time in a evacuated jig at a pressure of 10^-3 torr. After polarizing for one hour at the desired temperature, the sample was cooled to room temperature under the constant field application, then the electrodes are shorted for about 5 minutes to
Fig. 3.4

Diagram:

- Regulated Power supply
- Digital Microvoltmeter
- Film
- Electrometer
Fig. 3.5 Schematic sketch of an Experimental Jig used for electrical measurements.
remove stray charges on them. Now the samples were linearly heated up to a certain temperature with a uniform heating rate of 0.12 K/S and the current was measured using an electrometer amplifier (kiethly 617 C). This current is known as thermally stimulated depolarization current (TSDC).

3.3.7 Pyroelectric Current

The experimental set up for measuring the pyroelectric current was the same as that used for the TSDC measurements. The pyroelectric current of CAB films was studied in the sandwich configuration using an evacuated jig at a pressure of $10^{-3}$ torr. The films were poled at a desired temperature and different polarizing field strengths. After poling, the film was cooled to room temperature and then shorted for 5 minutes much the same as that of TSDC. The first thermal run may be called depolarization or irreversible cycle. All the subsequent thermal cycles, that is, heating the short circuited sample at a constant heating rate to a desired temperature and subsequent cooling to room temperature give "reversible" or true "pyroelectric current".

3.3.8 Dielectric Properties

The experimental set up for the measurement of dielectric properties is shown in Fig. 3.6. The dielectric film was mounted in an experimental jig (Fig 3.5) which was placed in a vessel evacuated to a pressure of $10^{-3}$ torr. The dielectric capacitance and Dissipation Factor, tan $\delta$, measurements were made on well annealed experimental film with a GenRad Digibridge (model 1689) in the low frequency range $10$ Hz.
FIG. 3.6 PHOTOGRAPH OF EXPERIMENTAL SET UP FOR THE DIELECTRIC MEASUREMENTS
- 100 KHz and with a Hewlett packard (model 4275A) in the high frequency range 10 KHz to 10 MHz. The range of temperature measurements was 300 to 450 K. The temperature was monitored by a copper-constantan thermocouple kept in the close vicinity of the experimental film.

3.3.9 Optical Absorption Spectra

The optical absorption spectra in the wave length range of 200-500 nm were recorded on peeled films of pure and 1 Wt% iodine-doped CAB, of thickness approximately 10 μm. From the spectra the absorption edge and optical energy gaps are evaluated to correlate with electrical conductivity measurements.
REFERENCES