CHAPTER - II

EXPERIMENTAL METHODS FOR FORMATION OF Al_2O_3 AND STUDY OF PROPERTIES

This chapter deals with the experimental methods used for

* Deposition of aluminium on glass
* Preparation of Al_2O_3 thin films
* Measurement of thickness
* Refractive index measurement
* Adhesion measurement
* Measurement of D.C. Resistance
* IR and XRD studies
* Effect of moisture and heat

2.1 DEPOSITION SYSTEM :

There are many methods available for deposition of aluminium films, vacuum thermal evaporation is found to be most suitable. This method was adopted for deposition of Al films. The performance of vacuum system is the most important consideration for the vacuum deposition of films. Using a good vacuum influences the properties of the evaporated material.

The system used for this work is Hind Hivac system model No. 12A4D with a direct drive rotary pump and 4 1/2"

oil diffusion pump to get a vacuum better than $8*10^{-6}$ Torr in a 12" glass dome. The photograph is shown in Fig.2.1. The steel base plate had 12 port holes for electrical feed throughs, air admittance valve and penning gauge head. The glass dome was kept on it with a thick neoprene L gasket acting as a seal. A thermocouple- pirani gauge assembly was employed to measure backing pressure (~ 10^{-3} Torr) and chamber pressure (10^{-3} - 10^{-6} Torr). The pump down time was nearly 1 hour for a vacuum of ~ $8*10^{-6}$ Torr. The electrical connections to the filaments are provided by a transformer 8 volt, 200 amps.

2.2 SUBSTRATE CLEANING :

The substrate used in this works were of size 75*25 mm (Micro Aid Micro Slides Deluxe Brand) of about 1 mm thickness.

The adhesion and purity of vacuum deposited thin films depends on the cleanlines of substrate. The substrate were washed in running water. Then they were kept in dilute chromic acid solution. After light rubbing in chromic acid, the substrates were cleaned in running water and then by scrubbing with cotton using soap solution (Balzer substrate cleaner) for removing greasy particle if any present. These were then washed in running water. Later the washing was done 3-4 times in distilled water. The substrates were handled by holding them at the corners with

stainless steel forceps. Then they were dried under infra-red lamp and then transferred inside the vacuum coating chamber.

2.3 ALUMINIUM FILM DEPOSITION :

The metallic aluminium (Balzer 99.99%) films of various thickness were deposited by resistive heating method, where the material to be evaporated is kept in an electrically heated filament. The evaporation source used was of tungesten in the form of spiral.

The glass substrates were kept on substrate holder made of aluminium with slots at the height of about 22 cm from the source. For thickness measurements and refractive index measurements, sharp stainless steel blades were used as mask for sharp demarcation.Provision of masking was made in substrate holder for Adhesion, D.C. resistance, IR and XRD studies.

2.4 Al_2O_3 FILM PREPARATION :

Al_2O_3 thin films can be formed using different techniques. But for our work as we had to obtain porous films the process of oxidation of Al films by keeping Al films in hot water and also by passing steam over Al films were adopted.

2.4.1 HOT WATER OXIDATION :

Al_2O_3 H_2O films were obtained by the oxidation of

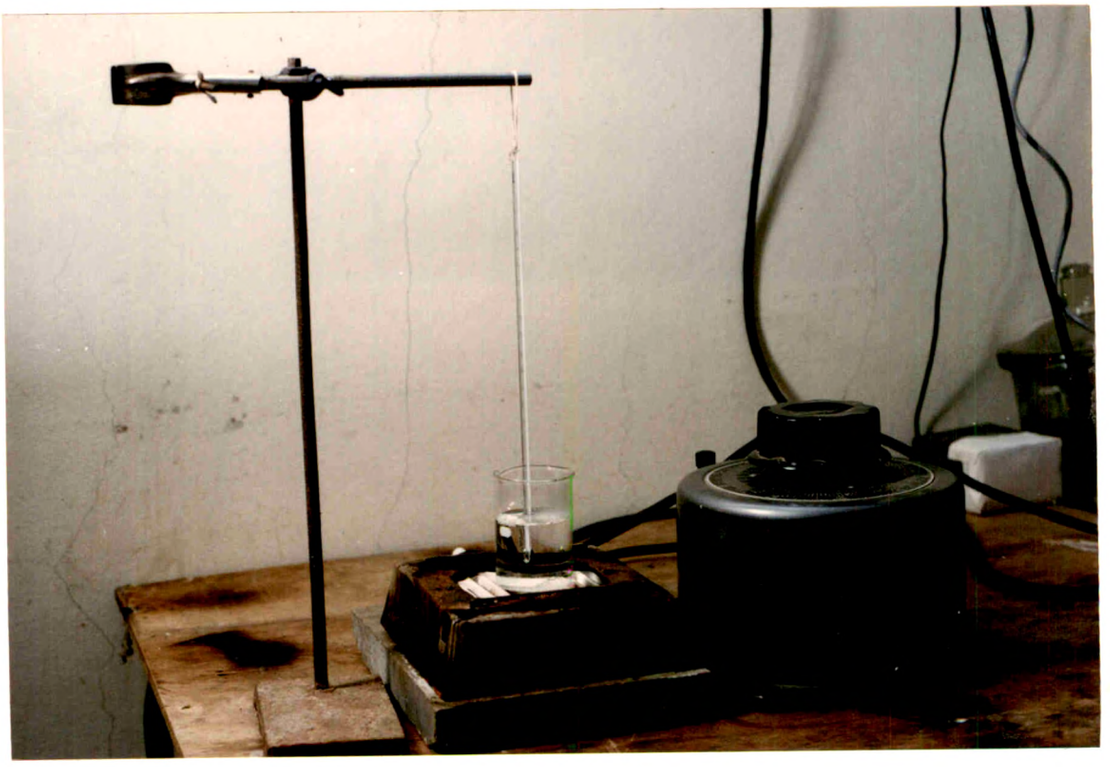

Fig. 2.4.1 SYSTEM FOR HOT WATER OXIDATION.

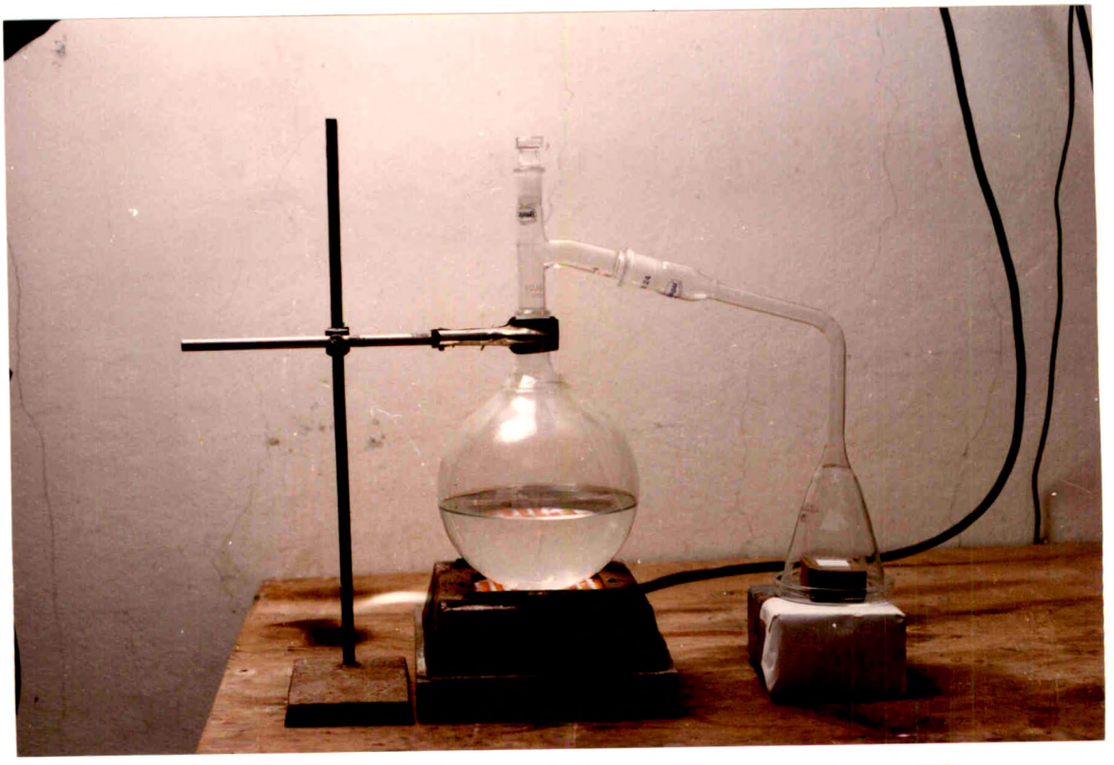

Fig. 2.4.2 SYSTEM FOR STEAM OXIDATION.

fresh Al films in warm distilled water maintained at temperature of 58°C[18]. Fig. 2.4.1 shows the photograph of oxidation cell arrangement. The beaker was filled with 200 ml of distilled water was raised and maintained at 58°C using a controlled heater. The Al films were introduced into the beaker. The evolution of hydrogen bubbles within a few minutes of immersion indicated the start of reaction with Al. Most of the Al disappeared within 10-12 minutes of immersion in water. Al_2O_3 films were removed from water and measurements were taken after drying in air.

2.4.2 STEAM OXIDATION :

In this process Al_2O_3 films were obtained by oxidation of aluminium by passing steam at 100°C over the film for 10-12 minutes as shown in Fig.2.4.2 . In this also the onset of oxidation could be seen from the disappearance of Al and the films becoming transparent. To the authors knowledge there are no reports of porous Al_2O_3 films obtained by oxidation of Al films under the steam environment.

2.5 THICKNESS MEASUREMENTS :

The thickness of Al_2O_3 films formed by both techniques were measured by Fizeau Fringes method[88]. This method works on the principle that when two reflecting surfaces are brought into close proximity, interference

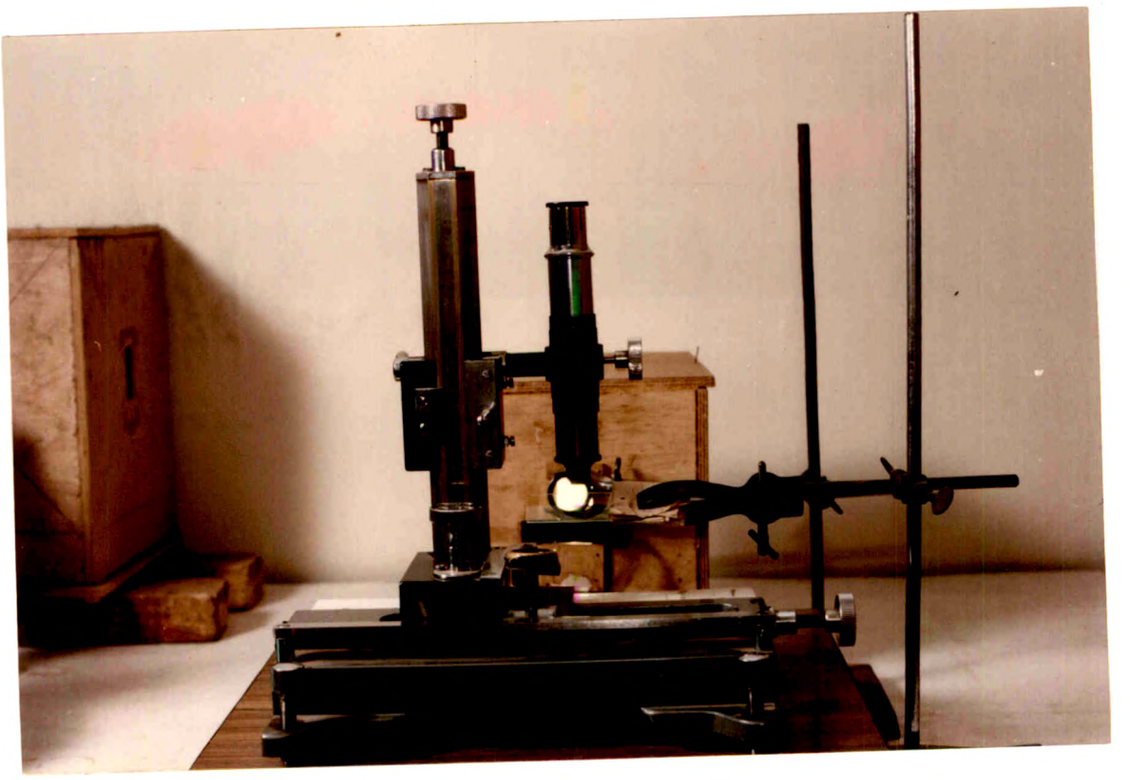

Fig. 2.5(a) SYSTEM FOR THICKNESS MEASUREMENT.

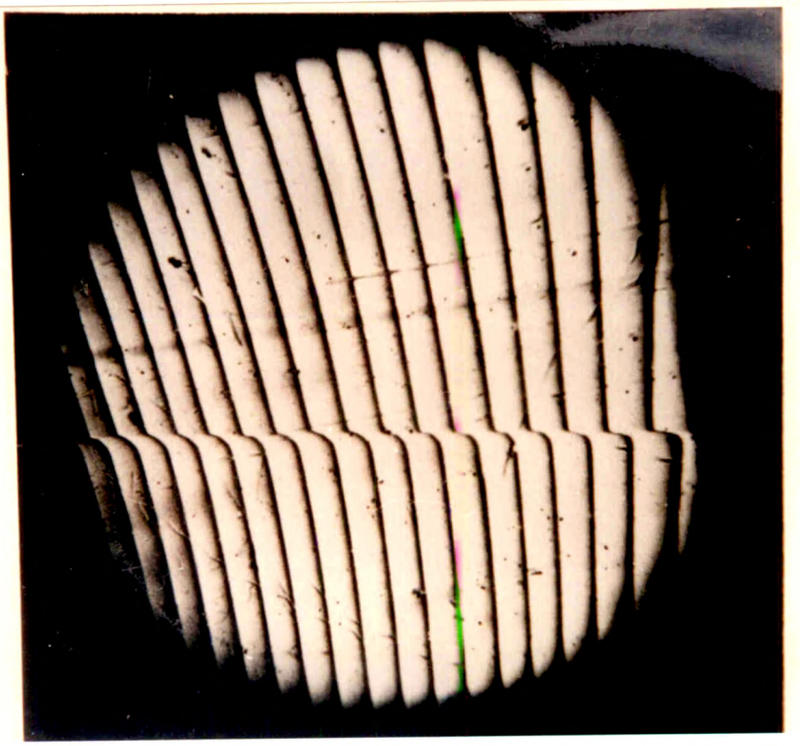

Fig. 2.5(b) FRINGES.

fringes are produced. The set up used is as shown in Fig.2.5(a) and Fig.2.5(b) gives the photograph of fringes. When an optical flat is brought in contact with film coated substrate, with the film forming a step and illuminated with a parallel monochromatic beam (λ= 5460 A°) at normal incidence interference fringes are observed. On viewing it with a low power microscope, dark fringes are observed which trace out the points of equal air gap thickness. There is a shift in fringes at the film edge. The two adjacent fringes are separated by $\lambda/2$. By adjusting the relative position of flats manually, the fringes are made into straight lines perpendicular to the step.

The displacement of fringes at the film edge can be expressed as a fraction of $\lambda/2$ fringe spacing.

The film thickness is given by

$$d_f = \lambda/2 \ [d/D]$$

Here d_f = Film thickness

d = Fringe displacement

D = Distance between fringes

λ = Wavelength of light.

2.6 ABELE'S METHOD FOR FINDING REFRACTIVE INDEX :

To find the refractive index of films Abele's method was used. The spectrometer having least count of 20'' was used and is shown in Fig.2.6. The spectrometer was initially aligned to get the plane of polarisation of

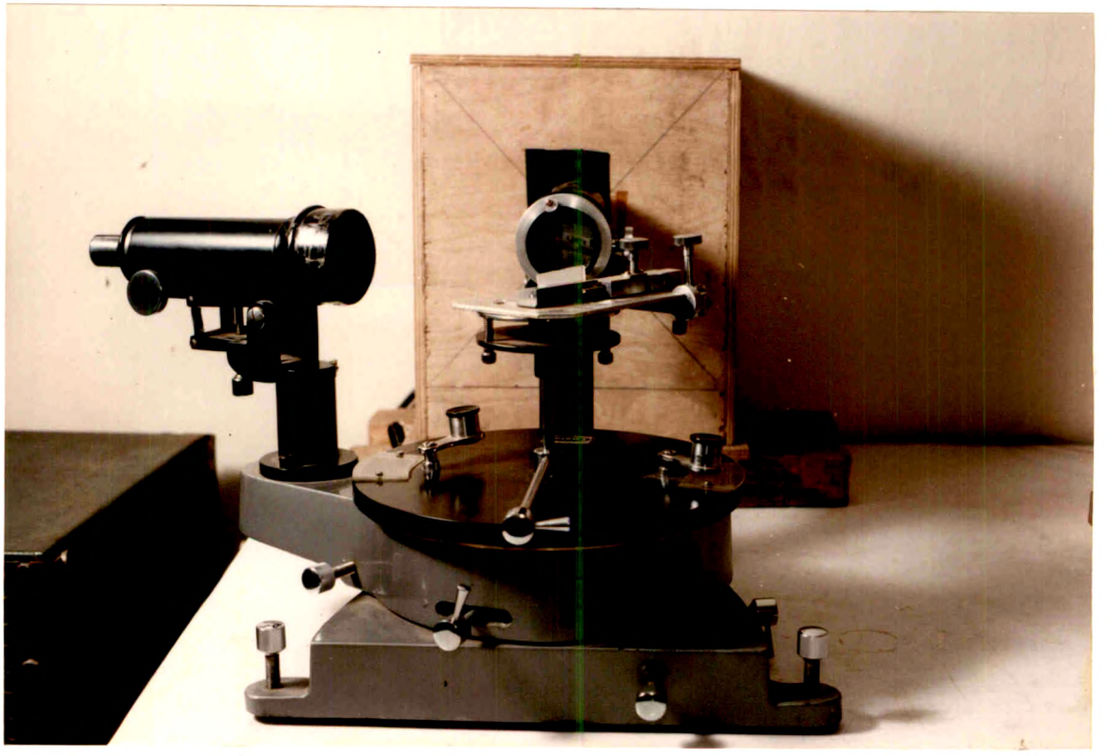

Fig. 2.6 SYSTEM FOR REFRACTIVE INDEX MEASUREMENT.

incident light in the plane of incidence, for which initially the Brewster angle, angle of glass was found. Sheet polaoid was used as polariser.

For this method half of the substrate was coated with the film. The film was fixed on a substrate holder having provision of three dimensional movement. To measure the angle of incidence accurately a cross wire was fitted very near to objective of the telescope.

The eye piece was removed and the cross wire was made to coincide with the substrate film demarcation. Further the angle of incidence was adjusted till the illumination from substrate half and the film half were equal. The adjustment was done a few times till the cross wire the centre of slit coincides with demarcation.This angle and the straight reading was noted and the angle of incidence found. The tangent of this angle gives the refractive index of the film. The accuracy of the measurement was 0.001 .

2.7 ADHESION MEASUREMENT :

There are various method for measuring the adhesion as discussed in article 1.7.

To measure the adhesion, Direct pull off method was used as shown in Fig.2.7(a). It consists of two chucks aligned on the same axis with one movable and other fixed. The movable end is attached to a spring balance of maximum

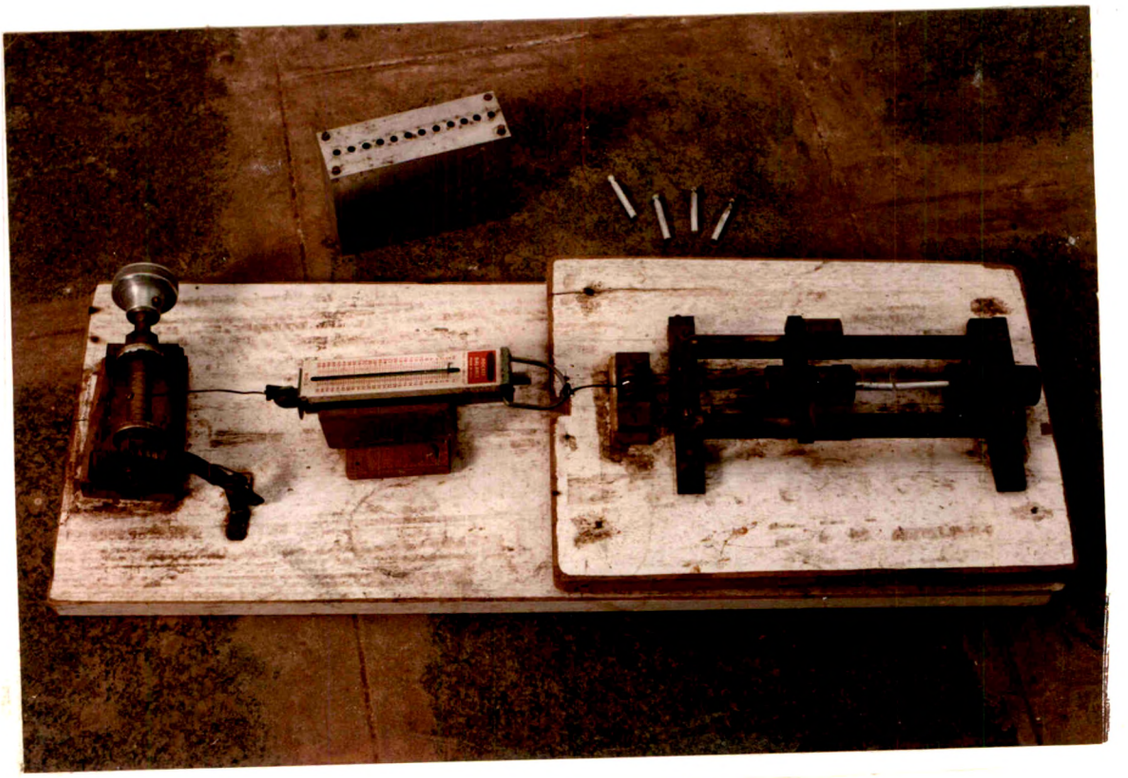

Fig. 2.7(a) SYSTEM FOR ADHESION MEASUREMENT.
(DIRECT PULL OFF METHOD)

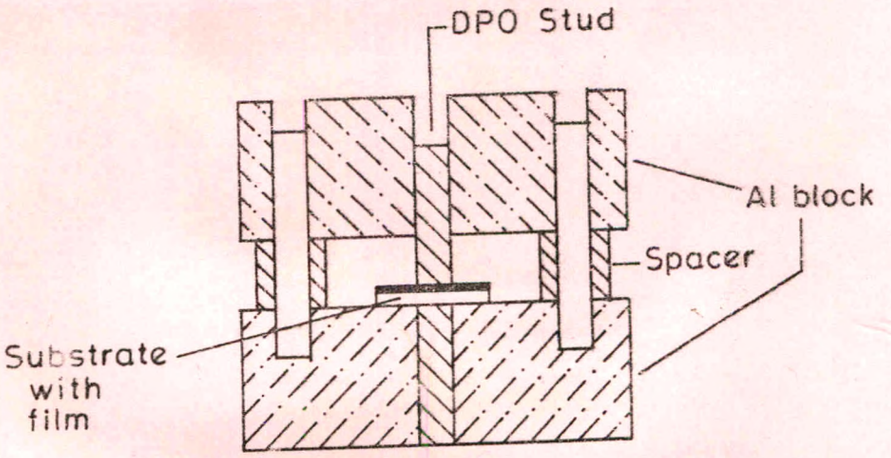

Fig. 2·7(b) - SAMPLE HOLDER FOR STUD
ALIGNMENT.

capacity of 50 Kg with accuracy ± 0.5 Kg. The spring arm of the balance is attached to pulling mechanism.

The samples are prepared on glass substrate of size 10x25 mm. For adhesion testing Al studs of diameter 0.5 cm and length 5 cm are attached to the film side.

The film coated substrate is than placed on the lower stud with the film side up. Then the top stud via the guiding hole is lowered into the film and pressed with Araldite drop betweeen stud and film. For complete curing of adhesive the samples are kept in the fixture for 24 hours as shown in Fig.2.7(b).

The stud with glass side is attached to the fixed chuck of tester and coated side stud to movable chuck. By gradually increasing the tension by pulling mechanism, a fracture occurs in the samples from film substrate interface. If the fracture occurs from glass side then the value is taken as the minimum limiting value for the adhesion.

To calculate the force of adhesion per unit area, the spring balance reading x Kg is noted. The area (A) is taken as adhesion α_A in KgF/cm^2 is obtained by

$$\alpha_A = \frac{(x * g)}{A} \; KgF \; cm^{-2}$$

g = acceleration due to gravity = 9.8 m/sec^2

2.8 SYSTEM FOR D.C. RESISTANCE MEASUREMENT :

A planer resistance configuration was used to study the D.C. resistance of Al_2O_3 films. The dimension of the resistor film on a alumina substrate was 2.5 * 0.5 cm as shown in Fig.2.8(a). Vaccum evaporated aluminium films was used as electrodes. The distance between the electrodes was the dimension of the resistor film. Crocodile clips with Al foils was used to connect to the meter and power supply. For measurement, two probe method as shown in Fig.2.8(b) was used. For all the measurements a constant voltage of 4 volt was used. The current was measured by Digital Picoammeter Model No.DPM - 111 of Scientific Equipment Co. With an accuracy of ± 0.25% for all ranges.

Resistance = V/I ohm

2.9 SYSTEM FOR AGING STUDIES :

2.9.1 SYSTEM FOR EXPOSURE TO HUMIDITY :

Al_2O_3 films were exposed to only one humidity level. This humidity chamber for obtaining the saturated humidity level ~ 98% at room temperature consists of a glass vacuum dessicator of 6 inch diameter filled with water upto 6.5 cm height.The films were kept in petri dish. The petri dish was placed 4 cm above the water level with the help of metal support as shown in Fig.2.9 .

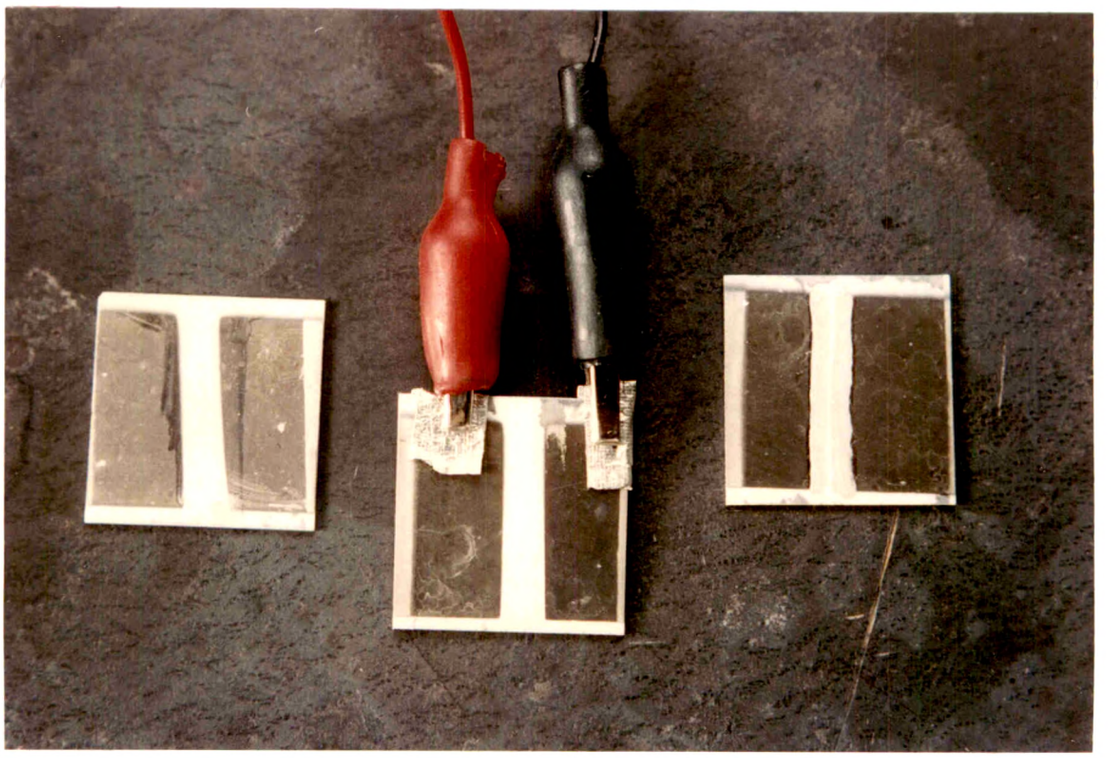

Fig. 2.8(a) PLANER RESISTOR ON ALUMINA SUBSTRATE.

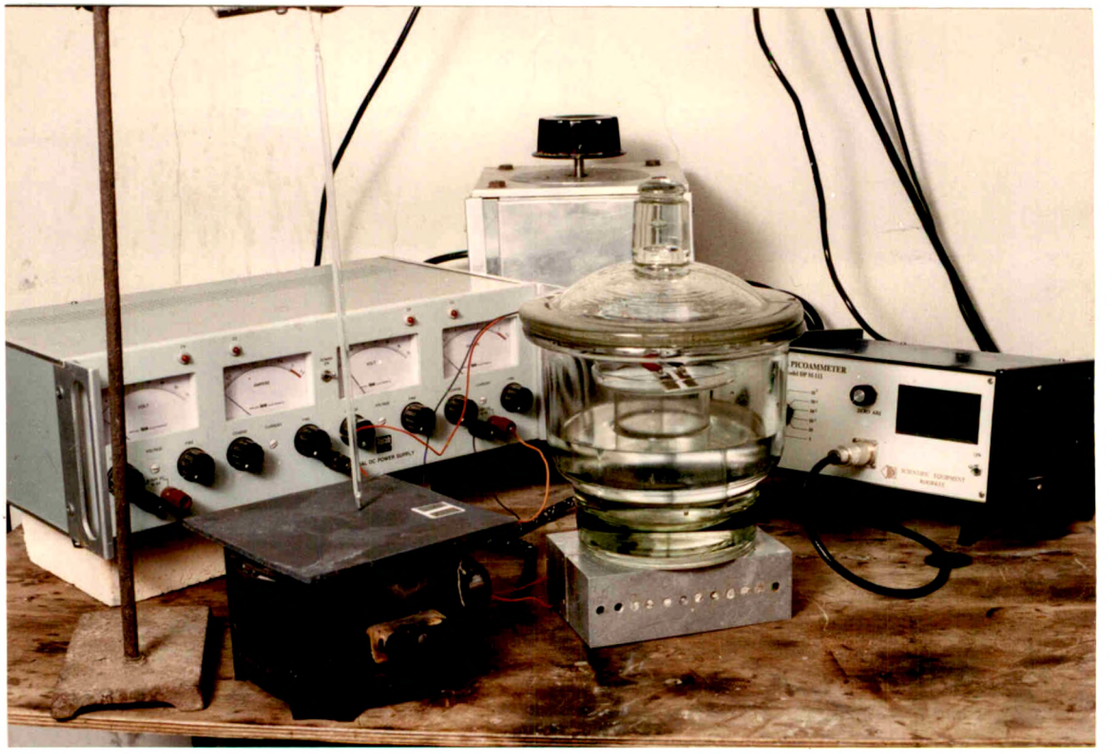

Fig. 2.8(b) SYSTEM FOR RESISTANCE MEASUREMENT.

The system equilibrium time was very large of the order of one hour, therefore the films were kept in chamber for 3 hours, so that the complete system i.e. Al_2O_3 films and the surrounding are in equilibrium condition. The other various measurements i.e. refractive index, adhesion, IR were taken with in a period of 30 minutes after removing from the chamber.

2.9.2 SYSTEM FOR EXPOSURE TO HEAT :

The heater is shown in Fig. 2.9. The temperature of heater was maintained at 120°C with dimmerstat. A thick Aluminium sheet was placed above the heater and samples were kept on it. The samples were heated for 3 hours. After the films attained room temperature reading were taken.

2.9.3 SEQUENCIAL EFFECT STUDIES :

The films were cycled in the following sequence heated at 40°C for 30 minutes -- 65% humidity for 30 minutes --98% humidity for 30 minutes -- exposure to atmosphere for 30 minutes, and refractive index measurement were taken after exposure to each ambient. These films were made to undergo this cycle 3 times. For D.C. resistance measurement the films were cycled for following sequence

a) 98% moisture, 30 minute -- Heat 40°C, 30 minute-- Air (room temperature)

b) 98% moisture -- air -- moisture -- air

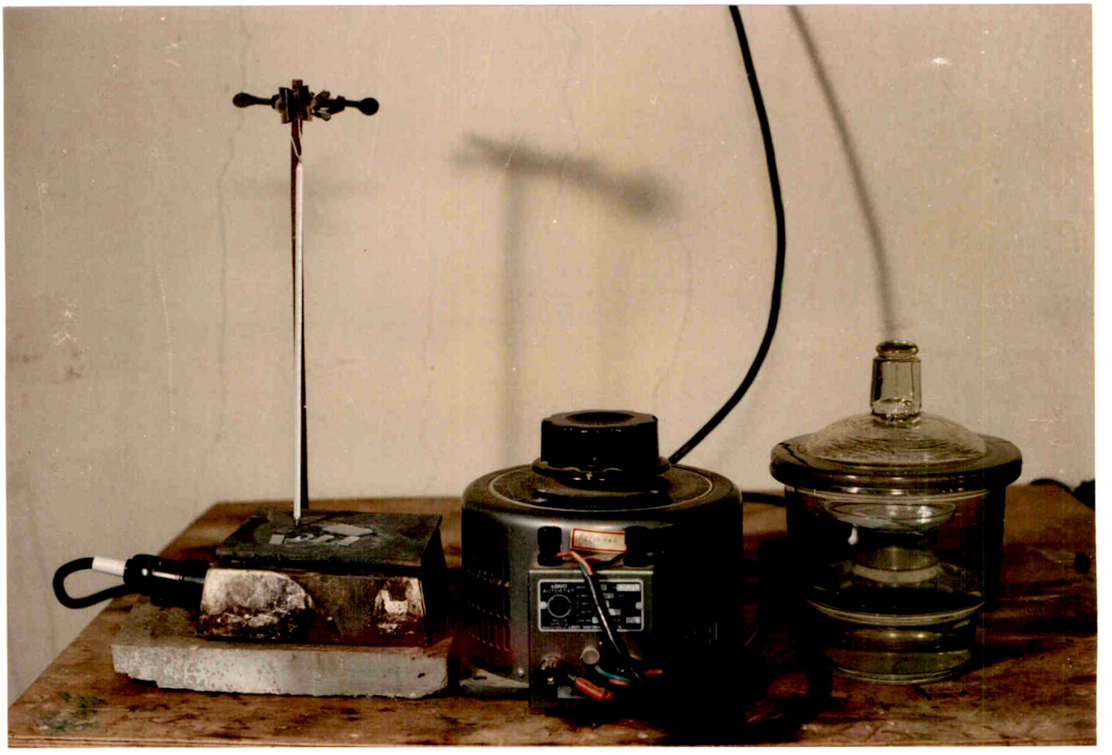

Fig. 2.9 SYSTEM FOR AGING STUDIES.

The substrate temperature of 40°C was maintained with the help of heater (controlled by dimmerstat).

2.10 IR AND XRD STUDIES :

The IR plots of the Al_2O_3 films were taken on Perkin Elmer 783 IR Spectrophotometer at USIC, Shivaji University, Kolhapur.

Though the IR-spectrophotometer has a provision of scanning wave number 4000-200 cm^{-1}. For our work we took the scan from wavenumber 4000 to 2000 cm^{-1} due to the absorption of glass substrate beyound 2000 cm^{-1}. The sample size for IR was 2.5 cm * 2.5 cm and the film coated substrate was kept in the path of the beam. Care was taken that the IR completely pass through the film. The out put was recorded on the chart paper.These studies were mainly done to determine the presence of moisture in the films from the absorption bands.

Since no other substrate was available which showed Transmittance in the 1696-1345, 1162-900 cm^{-1} bands to actually study the water absorption, glass was used which gave around 42% Transmittance at 3340 cm^{-1}.

The XRD was taken using low angle, Regako Rotaflex RV 200B diffractometer using Cu-Kα, λ = 1.5418 A^{o} at Poona University. XRD of only fresh films were taken. The formation of Al_2O_3 was confirmed by X-ray diffraction data.