CHAPTER II

DEPOSITION OF CERIUM OXIDE FILMS AND PROPERTY STUDIES

2.1 EXPERIMENTAL METHODS

This chapter deals with the experimental methods used for deposition of ceriue oxide on glass substrate. The thermal evaporation method under vacuum was used for deposition. Sufficient care was taken to get films of good quality. The samples were kept in different ambients, viz. air, room temperature moisture, cold moisture, salty moisture and heat .The change in adhesion, stress values, and (Δ),(Ψ) are studied using adhesion tester, stress measurement instrument and ellipsometer.

The structure of the films are often sensitive to the condition of preparation viz. the temperature of the substrate, the rate of deposition, pressure in the evaporator etc. These were, therefore, kept constant throughout these experiments. The measurement of the film thickness is also required to be carried out carefully as it plays a dominant role in the effective optical and mechanical properties of the films. This chapter deals with the arrangements utilised for the deposition of nonchopped and chopped films. The different ambient conditions produced in the laboratory are also explained.

2.2 VACUUM SYSTEM USED FOR DEPOSITION

In this work the conventional vacuum system (HIND HIVAC MODEL NO - 12 A 4 D.) with a rotary pump and 4.1/2" oil diffusion pump is used to get a vacuum of better

than $8 * 10^{-6}$ torr in a 12" glass dome. The photograph of vacuum system is shown in fig. 2.2. The tungsten boats and also molybdenum boats were used for the evaporation of substances.

In this system the glass dome (Corning) which was the deposition chamber was kept on a steel base plate sealed with a thick neoprene L - gasket. The base plate had 12 port holes for electrical feed throughs, air admittance valve and penning gauge head. A pirani - penning gauge assembly was employed to measure backing pressure ($\sim 10^{-3}$ Torr) and chamber pressure ($10^{-3} - 10^{-6}$ Torr). The pump down time was nearly 1 hour for a vacuum of $\sim 8*10^{-6}$ Torr. The electrical connections to the boat was provided by a transformer 8 volts - 200 amps.

2.3 SUBSTRATE USED AND ITS CLEANING.

It is well known that the irregularities of the surface of the substrate has important effects on the properties of the film deposited on it. The substrates used in the present experiment were of size 75 * 25 mm (Micro Aid Micro Slides Deluxe Brand) of about 0.8 mm thickness. In order to avoid reflection from the back surface of the substrate, the back surface was grounded. The roughening was done by means of fine grain emery powder taking care not to scratch the other surface. The refractive index of this substrate was 1.56 (as found by Abele's method).

The adherence and purity of vacuum deposited

thin films depends on the cleanliness of the substrate in use. The thorough cleaning of the substrate prior to deposition is, therefore, absolutely necessary. The macroscopic impurities were removed by washing in running water and soaking the substrates in dilute chromic acid for 15 - 20 minutes. They were lightly rubbed with cotton and again kept under running water. Degreasing was done by scrubbing them with cotton using hot soap solution taking care not to cause scratches. In order to remove the traces of soap solution rinsing in lukewarm distilled water was done. The washing in distilled water was done 3 to 4 times for 3-5 minutes each. During all these processes the substrates were handled by holding them at the corners with stainless steel forceps. They were dried under an infrared lamp and transferred inside the vacuum coating chamber.

2.4 METHOD OF FILM PREPARATION.

The material CeO_2 was in the form of granules of high purity 99.999% obtained from Balzars Ltd. The choice of the evaporation methods depends on the required results, on the equipment available and on the coating material. The most frequently used method is resistive heating, where the material to be evaporated is kept in an electrically heated boat of a high melting point material. The evaporation source used here was tungsten or molybdenum shaped into a boat.

Single films were deposited in one evacuation cycle. For all depositions, the substrate holder used was

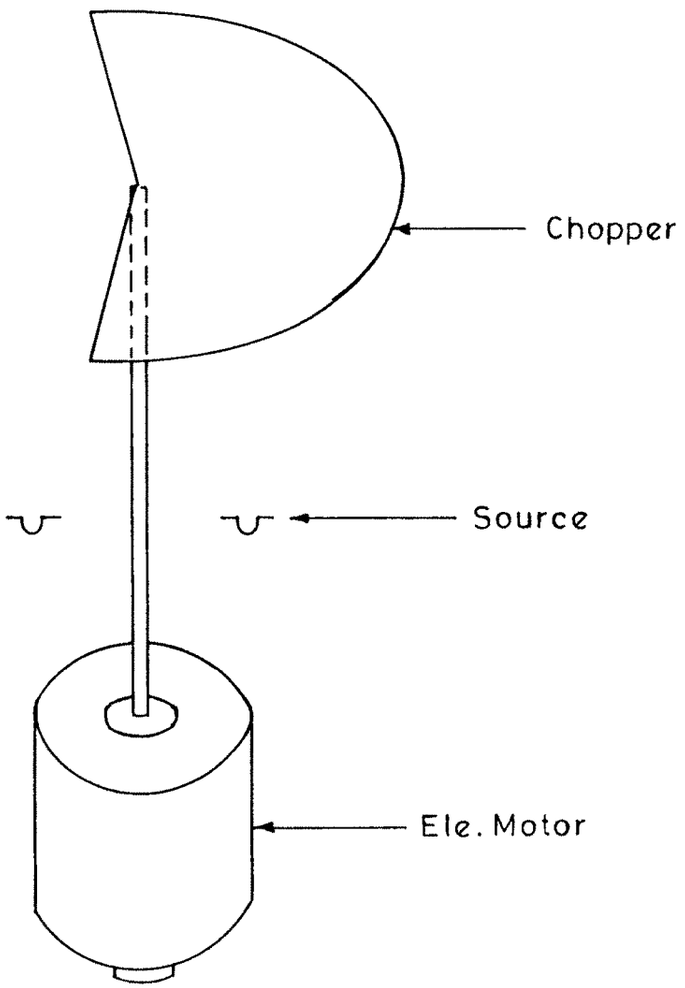

Fig. 2·4·1 – Chopper.

made of aluminum with slots on the top at a height of about 22 cm from the source. Sharp edged stainless steel blades were used as masks for thickness measurement samples.

2.4.1 SINGLE FILM BY CHOPPING.

The chopper was made of a light aluminium vane attached to a motor. The small motor was fixed inside an aluminium container with a broad base to be kept on the base plate inside the vacuum chamber. The speed of rotation was controlled from outside the vacuum chamber by means of a TPSU. The shaft of the motor was attached to a light aluminium hollow rod of 8 cm in height to which the vane of chopper was fixed. The vane was made of a very thin metal sheet act into a circular shape of 12.5 cm diameter which as given a 'V' cut, as shown in fig. 2.4.1. The chopping rate of about 5-6 rot/sec was maintained in all the experiments.

2.5 SYSTEM FOR THE AGING STUDIES

The films deposited by using the various techniques mentioned above were subjected to treatments under various ambient conditions. The films were kept in various ambients for a fixed period of time and the readings were taken after taking it out of the ambient conditions. For producing controlled environmental conditions different types of setups were made to suit the required experiment.

2.5.1. SYSTEM FOR STUDY UNDER MOISTURE AT ROOM TEMPERATURE CONDITIONS.

The chamber for studying the effect of moisture,

consisted of a glass vacuum dessicator of 6 inch diameter filled with water upto a height of 6.5 cm. The petri dish containing the films were kept on a metal support at a height of 6 cms. above the water level as shown in fig. 2.5.1. The vacuum dessicator provided the air tight container and about 98% humidity atmosphere inside the chamber.

2.5.2. ROOM TEMPERATURE MOISTURE _ 3 _ HOURS-AIR.

Here after the initial readings of the fresh films were taken, they were kept in the humidity chamber for ' 3 ' hours. The time of ' 3 ' hours was found sufficient for equilibrium to be attained in the system. The films were taken out, adhesion and ellipsometric readings (Δ) and (Ψ) were measured in air. The films were then kept in air to measure (Δ), (Ψ) after six months .

2.5.3. SYSTEM FOR STUDY UNDER COLD MOISTURE.

For this system the samples were kept in closed petri dish and kept in shelf nearest to the freezer in a refrigerator at temp 8 ^{o}c for ' 3' hour's. After ' 3' hour's the films were taken out and then readings were taken.

Some of the samples were then kept in air to measure (Δ) , (Ψ) after six months.

2.5.4 SYSTEM FOR STUDY UNDER SALTY MOISTURE AT ROOM TEMPERATURE.

The dessicator system similar to that mentioned in 2.5.1 was used. Here instead of water a 50% concentrated

sodium chloride solution was filled upto 6 cm from the base. This provided a saturated salty atmosphere. Here also the films were kept under the exposure sequence, moisture ' 3 ' hour's - air. The readings for Ellipsometer were not taken.

2.5.5 SYSTEM FOR STUDY ON HEATING.

The heater shown in fig. 2.5.1 was used to heat the films to 120 °c for ' 3 ' hour's, with the help of Dimmerstat the temperature was controlled. A thick aluminium sheet was kept on the heater and samples placed on it. The variation in the temp. was around ± 5 °c.

After ' 3 ' hour's heating, the films were allowed to cool and then the readings were taken.

2.6 THICKNESS MEASUREMENT.

When two reflecting surfaces are brought into close proximity, interference fringes are produced, which make possible the measurement of thickness of the film. In this work thickness of the film was measured by Fizeau fringes,[3] using multiple beam interferometry. The interferometer is the normal standard one, consists of two slightly inclined optical flats, one of them supporting the film, which forms a step on the substrate. When the second optical flat is brought in contact with the film surface, and the interferometer is illuminated with a parallel monochromatic (λ = 5460 Å) beam at normal incidence and viewed with a low power microscope, dark fringes can be observed which trace out the points of equal air gap

thickness. The two adjacent fringes are separated by (λ)/2.

Fig. 2.6 (a) shows the photograph of the arrangement and fig. 2.6 (b) gives the photo of fringes. By adjusting the relative positions of the flats to form a wedge shaped air gap, the fringes can be made into straight lines perpendicular to the steps on the films by manual adjustment.

The fringes show a displacement as they pass over the film step edge. This displacement expressed as a fraction of the (λ)/2 fringe spacing gives the film thickness,

$$d_f = [(\lambda) / 2] [d / D] \qquad 2.6$$

where,

d_f = film thickness.

d = fringe displacement.

D = distance between fringes.

λ = wavelength of light.

2.7 ADHESION MEASUREMENT.

The various methods for measuring adhesion has already been described in art 1.2.1. For this work, the Direct Pull Off method has been used.

The adhesion tester developed in the laboratory for Direct Pull Off method consist of two chucks aligned on the same axis with one movable and other fixed as shown in fig.2.7 (a). Chuck is attached to a spring balance with a maximum capacity of 50 Kg, with an accuracy of $\pm$ 0.5Kg. The

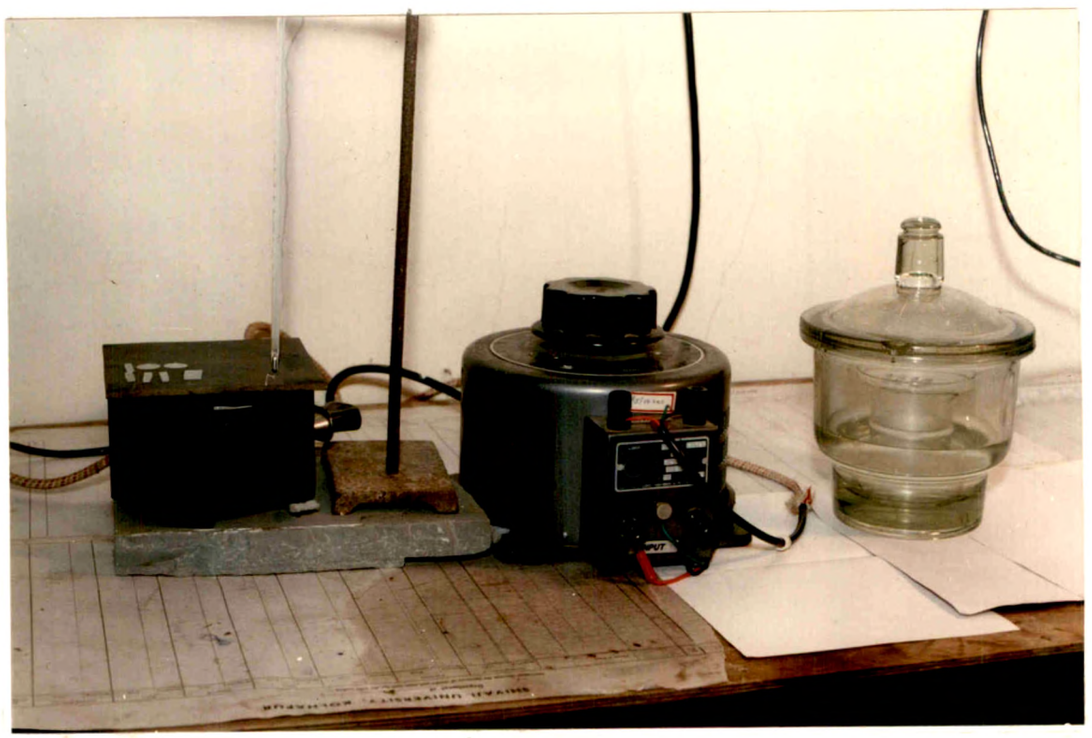

Fig 2.5.1 SYSTEM FOR THE AGING STUDIES

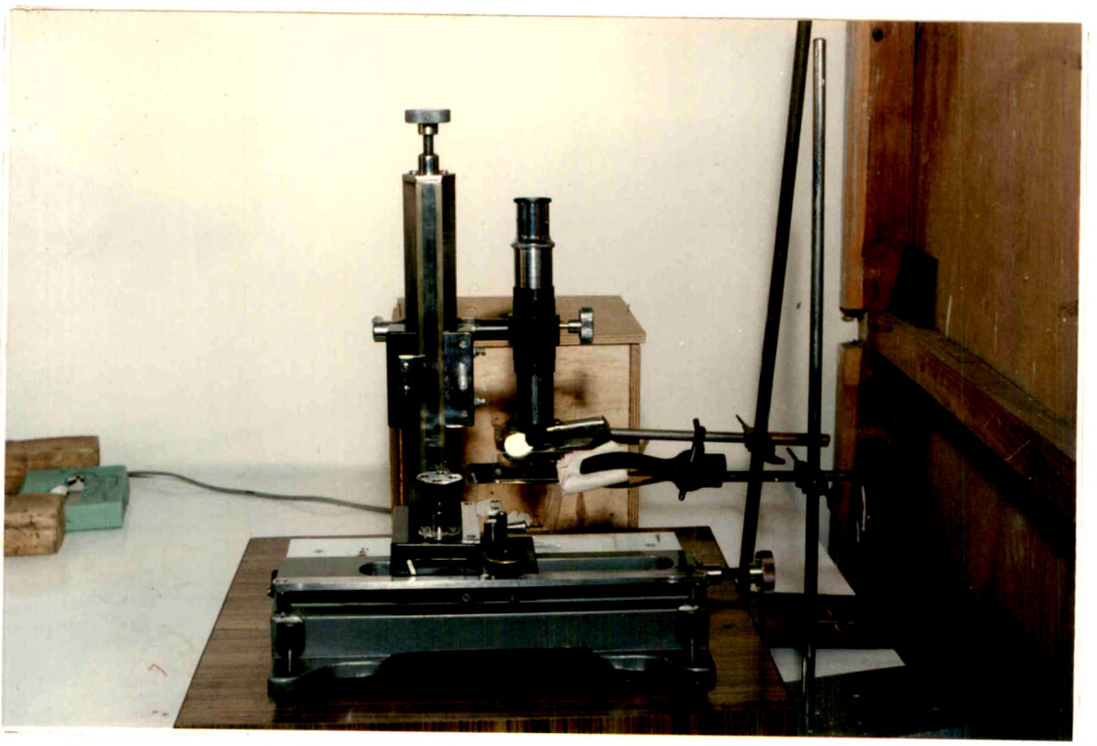

Fig 2.6 (a) ARRANGEMENT FOR THICKNESS MEASUREMENT

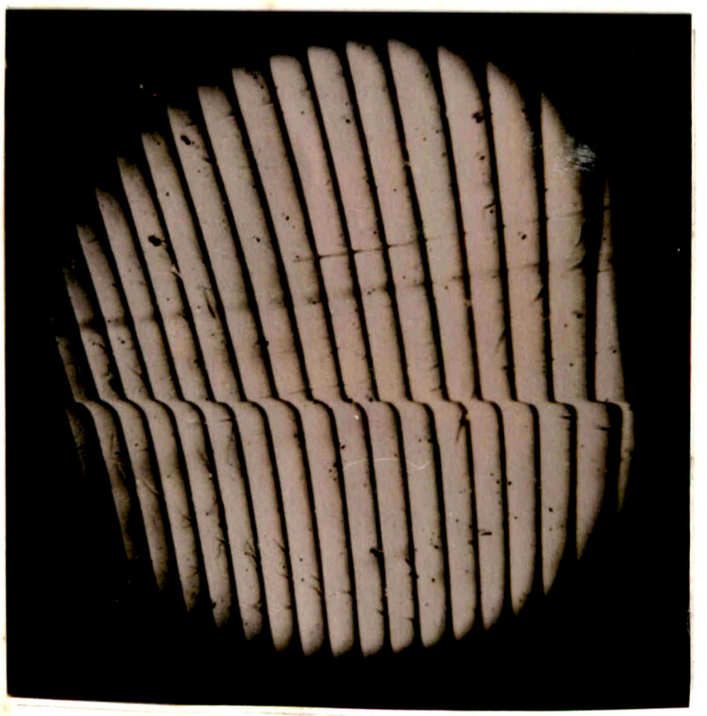

Fig 2.6 (b) FRINGES

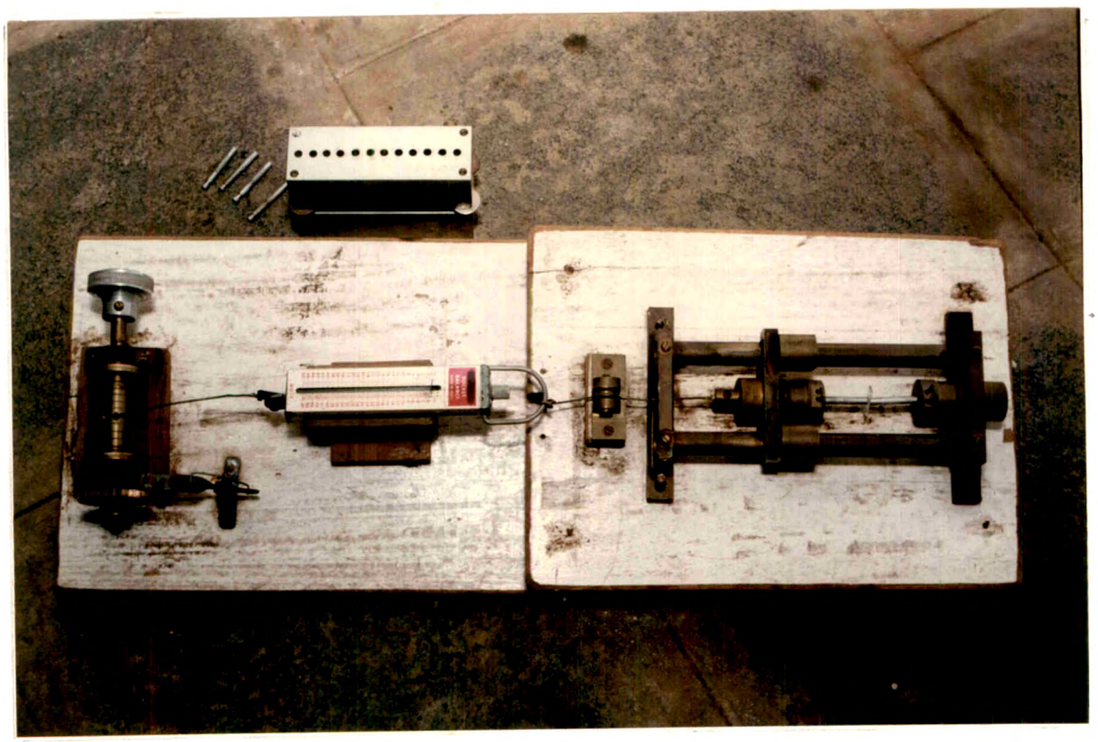

Fig 2.7 (a) ARRANGEMENT FOR ADHESION MEASUREMENT (DIRECT PULL-OFF METHOD)

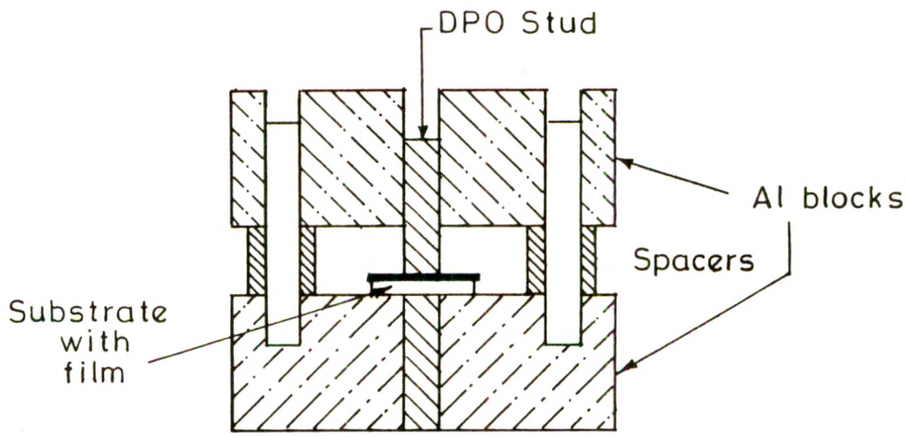

Fig. 2·7 (b) — Sample holder for stud alignment.

spring arm of balance is connected to a pulling mechanism through a cable.

The samples for adhesion measurement are CeO_2 coated glass substrates of size (1 cm * 25 mm, thickness : 1.3 mm + 0.1 mm). In order to prepare them for adhesion testing, Al studs of diameter 0.5 cm and length 5 cm are attached to the film side and backside of the glass with an adhesive " Araldite ".A special fixture (Fig 2.7 - b) is used so as to align the studs along an axis normal to the film plane. First, the lower stud is placed in the fixture and a drop of Araldite is placed on its surface. The CeO_2 coated substrate is then placed on the lower stud with the coated side up. Then the top stud with a drop of Araldite already on it, is lowered onto the film, via, guiding holes in the top part of the fixture. The top stud is lightly pressed to ensure uniform distribution of the adhesive between the studs and the contact areas of the sample under test. The samples are left in the fixture for a period of 24 hours so as to ensure complete curing of the adhesive.

The CeO_2 coated glass substrate with the Al studs attached to it is placed in the adhesion tester so that one stud is held by the fixed chuck and the other stud is held by the movable chuck.

Tension applied by the pulling mechanism is gradually increased at a uniform rate until fracture occurs in the sample under test. Fracture normally occurs at the

film substrate interface. However, at high adhesion values sometimes the fracture occurs at the Araldite glass or Araldite Al stud interface. In that case the value obtained is taken to be the minimum limiting value for the adhesion.

CALCULATION OF ADHESION (σ_A).

In order to calculate the value of the force of adhesion per unit area, the reading on the spring balance "X" Kg is noted. The area (A) over which the pulling force is applied is taken to be the area covered by the Araldite at the Araldite film interface. The film adhesion " σ_A " in KgF/cm^2 is then obtained as:

$$\sigma_A \; (KgF \cdot cm^{-2}) = (X.g)/A$$

where 'g ' = acceleration due to gravity (g = 9.8 $m.sec^{-2}$)

2.8 STRESS MEASUREMENT.

In this experiment the stress was measured by using interferometric method by measuring the curvature of a thin circular plate. The substrates used for this purpose was soda glass cover slips of diameter 2.2 cm and thickness 0.145 cm. The stress measurement set up and fringes are shown in Fig (2.8).

In order to obtain a measurable curvature due to film stress the glass substrate must be thin. Majority of the commercially available cover slips are not optically flat. However, few are intrinsically concave in shape. Coverslips of measurable curvature are selected by placing them on (λ)/ 10 optical flat and choosing the ones which

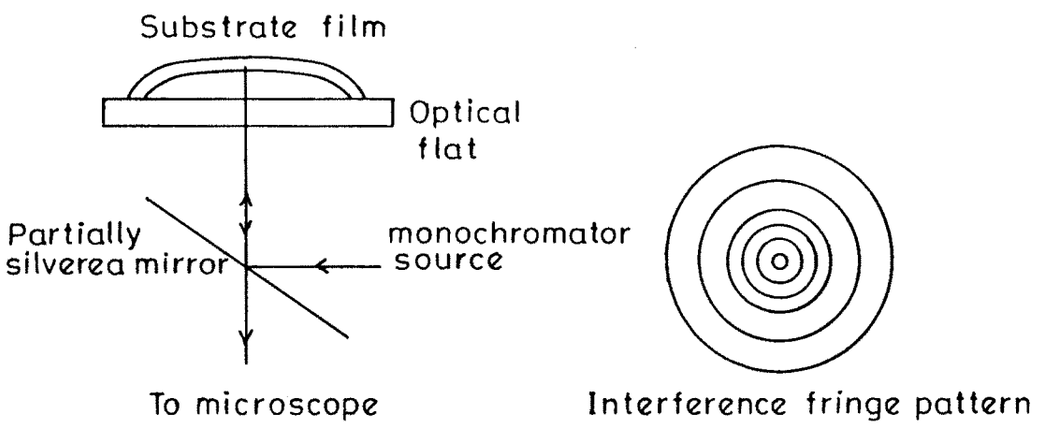

Fig. 2·8 Substrate curvature measurement by interferometry.

formed circular or oval fringes (Newtons rings) on being viewed in monochromatic light (λ_{na} = 5893 A^{o}) When the substrate is placed on the (λ)/ 10 optical flat and is lightly pressed and released, the fringe pattern moves first in and then out if the substrate is lying with its concave side down and vice versa, if it is lying with its concave side facing up. This occurs because the distance between the substrate and optical flat at a given point X which is responsible for the interference fringe formation in accordance with the equations.

$$2d = n\lambda \qquad \text{(minima)}$$

$$2d = (n+1)[(\lambda) / 2] \qquad \text{(maxima)}$$

The radius of curvature of the substrate is determined before and after film deposition in order to correct for the intrinsic curvature of the substrate. The fringe pattern obtained on placing the substrate (concave side down) on the (λ) / 10 optical flat and viewing it in monochromatic light of wavelength (λ) = 5893 A^{o} is measured using the traveling microscope. Light from a sodium vapour source (λ = 5893 A^{o}) is made incident normally onto the substrate placed on the (λ) / 10 optical flat using a partially reflecting surface S_1. Light reflected from the optical flat and from the substrate film surface interferes constructively or destructively and the resultant fringe pattern is viewed with the aid of a traveling microscope focused from the top.

From the fringe pattern the radii of the fringes are measured in the X and Y directions and plots of d_n versus r_n^2 are obtained as shown in graph 2.8 (1) where, $d_n = n(\lambda) / 2$ is the distance between the curved film and the optical flat, which is responsible for fringe of order 'n' and r_n is the radius of the fringe of order n.

The slopes K_x, K_y of the plots of d_n versus r_n^2 are related to the value of the tension per unit area Tx, Ty in the X and Y directions.

$$K_x = 3t\,(\,Tx - Ty\,) / Yh^2 \text{ and}$$

$$K_y = 3t\,(\,Ty - Tx\,) / Yh^2$$

and these are used to calculate the stress "S" in the film,

$$S = Yh^2\,(\,K_x + K_y\,) / 6t\,(\,1 - \nu\,)$$

$$Y = 7 * 10^{11} \text{ dynes/cm}^2$$

$\nu = 0.22$

t = film thickness cm

h = substrate thickness cm

Since the uncoated substrates are not totally flat but have a measurable curvature, the values of the slopes obtained for the uncoated glass are denoted by K'_x and K'_y. These are subtracted from the values (denoted by K''_x, K''_y) obtained for coated glass onto the curved substrates so as to obtain the correct K_x, and K_y values due to stress "S" in the film only.

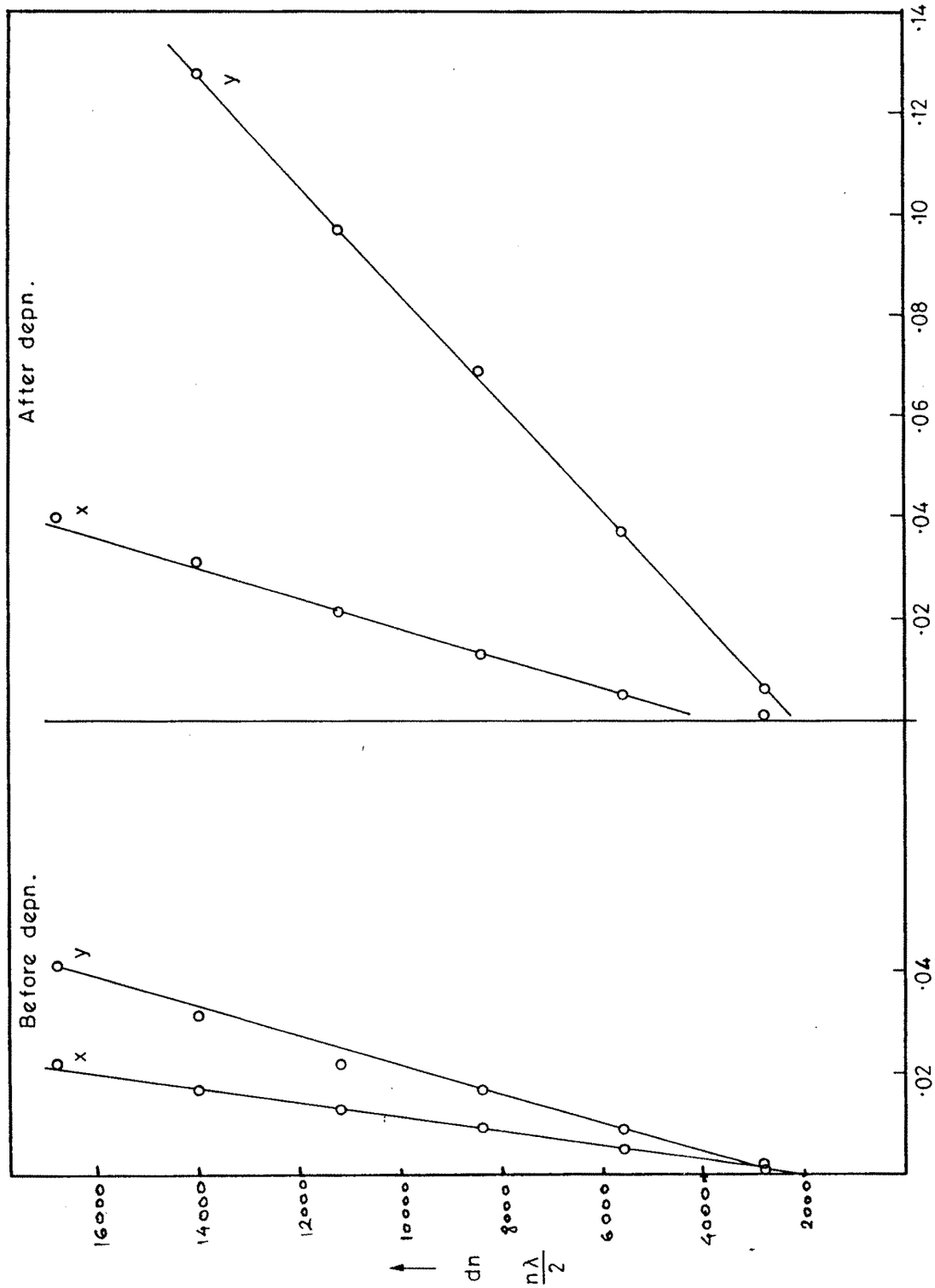

Fig. 2·8 (1) — Plot of dn versus rn^2.

2.9 DESCRIPTION OF ELLIPSOMETER USED.

An ellipsometer is basically a device to determine the azimuths. The basic requirements of an ellipsometer are monochromatic source, a polarizing device with provision for azimuth changing, a suitable quarter wave plate, mount for the reflector, an analysing device of reflected beam and a suitable detecting system. Fig 2.9 gives the photograph of the ellipsometer used.

An ellipsometer was designed and built in the laboratory by previous worker.[65] It consists of a spectrometer to which the polarizing and analyzing systems are attached to the collimator and telescope arm respectively. Two polariod sheets [Edmund scientific co., Barington, N.Jersey] each attached coaxially in a circular scale at 5.5" diameter served as the polariser and analyser. The scales are marked on the periphery. The vernier scale having 50 - divisions on each side of zero is kept fixed, while the main scale marked from 0^{o} to 360^{o} is rotated by hand for rough adjustment. For finer adjustments screws are provided on the main scale. The least count is 0.01 deg. The quarter - wave plate is mounted on a separate circular mount and supported from the polariser mount. The polariser, the quarter - wave plate and the analyser can be rotated independently in their respective mounts. The prism table of the spectrometer is used as the mount for the reflecting film sample.

The source of illumination is a low power

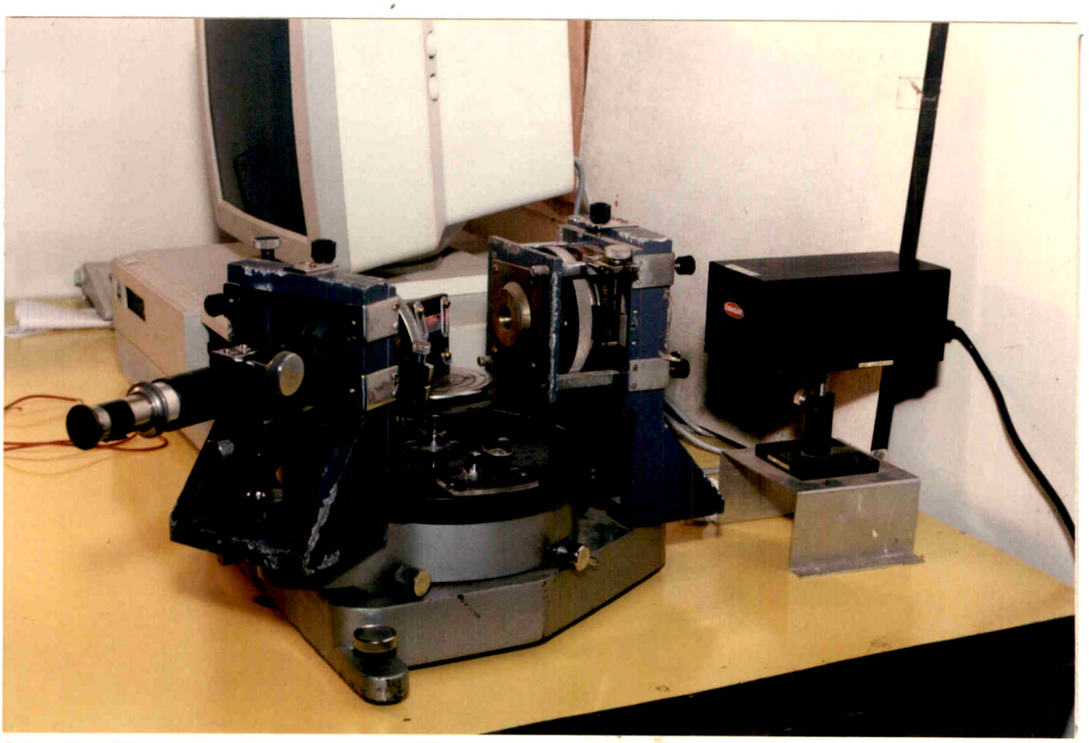

Fig 2.9 THE ELLIPSOMETER

(0.5mw) Helium - Neon laser of wave - length 6328 $\mathring{A}$. The choice of the laser beam as the source of light was due to two reasons.

1) If the monochromatic analysis for ellipsometery is to hold good, it has been shown by smith[127] that the optical bandwidth of the source must be small, so that only unique polarisation state will pass through the ellipsometer and better nulls could be obtained.

2) The high intensity of the laser source makes it very useful.

Visual detection of null was used with an accuracy of 0.06 deg. in the azimuth measurement. The alignment and calibration was done following the method of Archer[111].

2.9.1 EXPERIMENTAL PROCEDURE FOLLOWED.

All the ellipsometric observations were made in air at an angle of incidence of 50°. Each sample to be studied was adjusted on the prism table with the sample holder. The reflected image was made to coincide with the center of the cross wire of the telescope by adjustment of the sample position. The polariser azimuth (P) and analyser azimuth (A) were adjusted simultaneously, first with rough motion and then with fine motion screws, to give null intensity. (Δ) and (ψ) were measured from equation 1.6.1.16 and 1.6.1.17.