CHAPTER II

DESCRIPTION

I. EVAPORATION CHAMBER FOR EVAPORATION OF COPPER IN VACUUM ON QUARTZ SUBSTRATE:

The main features of the evaporation chamber are summarised as below:

1. Diffusion pump backed by suitable backing pump.
2. Phosphorus pentoxide trap to absorb moisture from the vacuum chamber.
3. High current, leak-proof terminals and a heating filament.
4. Rotatable leaf-type shutter.
5. Well cleaned substrate.
6. High tension discharge probes.
7. Vacuum gauge.
8. Suitable accessories like, pair of tongs, magnifying lens, linen pieces, benzene, alcohol, vacuum greases, plasticine, pine wax, etc.

(A) CONSTRUCTION:

A Cenco-megavac pump, in conjunction with a D. C. Motor (115 volts., 5 amps., ½ H.P. and 1725 R.P.M. : Emerson Electric Mfg. Co., N. Y.) is used as the backing pump which can produce a vacuum of 0.001 mm. with a suitable vacuum system. This pump
is connected to a glass tubing by rubber pressure tubing having a diameter 20 per cent less than that of glass tubing. The rubber tubing is previously boiled in caustic soda for four hours in order to drive out the adsorbed gases. A leak valve \( L \) having a small bore (0.1 mm.) is fitted at the top of glass tubing. Vacuum glass cocks \( C_1 \) and \( C_2 \) having 10 mm. bore are fitted at the inlet and outlet of the \( P_2O_5 \) trap, a vessel (12 cms. diameter 6 cms. height) at the bottom of which \( P_2O_5 \) is kept in a glass container. A thick glass plate together with a thin layer of plasticine, is used for sealing the top of the trap. An oil diffusion pump type \( Q \) (Leybold's Nachfolger A. G. Berlin) with the following specifications is used:

- **Pumping speed at** \( 10^{-4} \) mm. **Hg** = 20 litres/sec.
  
  (70-75 cbm./hour)

- **Heater input** ... ... = 450 watts.

- **Oil filling** ... ... = 75 ccm. Apiezon oil B.

- **Height** ... ... ... = 61 cms.

A Pirani gauge \( P. G. \) (Edwards & Co.) for measuring pressures up to \( 10^{-4} \) mm. and a tesla coil are used for hunting the leaks.

The evaporation chamber was designed and machined in the workshop. The procedures adopted in constructing the whole unit and attaining better the required vacuum less than \( 10^{-5} \) mm., are given in standard text books in vacuum technology (Strong, Procedures in Experimental Physics, Prentice-Hall Inc., New York, 1953; Yarwood, High Vacuum Technique, Chapman & Hall, London, 1948; Jnanananda, High Vacua, D. Van Nostrand Co., New York, 1947 and Dushman,
EVAPORATION CHAMBER AND KOHLRAUSCH BRIDGE
Vacuum Technique, John Wiley and Sons, 1949). The techniques involved in such evaporations are outlined by Olsen, Crittenden and Smith (50).

All the terminals are insulated from the brass plate (diameter 18 cms. and thickness 1 cm.). High insulation is obtained by neoprene rubber bushings from outside and thick mica rings from inside the vacuum system. Terminals 3 and 4 are of the rotary seal type (Fig. 1B) for leaf type shutter R and discharge probe D2 respectively. Terminals 5 and 6 are used for passing a current for the heating filament. These terminals are, therefore, connected to a Variac (current carrying capacity 6 amps.) through an ammeter (0-15 amperes A.C.). Terminals 1 and 2 are connected to the Kohlrausch Bridge for measurement of electrical conductivity inside vacuum. S is the substrate for depositing copper films. Three plates are used as substrates; 1) glass plate (2 cms. x 1.5 cm.) for depositing copper films for conductivity measurements, 2) quartz plate (1.8 cms. x 1.5 cm.) for reflection and transmission measurements, and 3) quartz plate (1.5 cms. x 1 cm.) only half of which is filmed, for thickness measurement, after proper silvering. These plates are placed near one another by a special mount so as to form a total area 4 x 3 sq. cms. at a distance of 10 cms. from the filament F having 8 turns. These plates were tested independently by transmission measurements for uniformity of thickness of copper film. This was observed to be so.
a leaf type shutter of aluminium. Actually two thin plates (one near the filament and the other near the substrate) coupled to the same rotary shaft are used. $D_2$ is a high insulation discharge probe with aluminium head. High insulation is attained by passing a thin wire (Fig. 1C) through a glass capillary which is sealed inside a hollow rotary shaft by balsein wax. $D_1$ is another terminal of the discharge probe. High tension (3 K.V.) supplied by induction coil is applied between $D_1$ and $D_2$. Filament $F$ is a molybdenum wire (diameter 0.4 mms. and 0.5 ohms./metre) coiled into a spiral (diameter 0.4 cms.) having eight turns. $Y$ is valve connected to pirani gauge ($P.G.$). A bell jar (25 cms. in height) sitting on a rubber ring gasket (Fig. 1A) at the circumference of the brass disc completes the vacuum system.

High grade copper (99.9 per cent purity) is used for evaporation purpose. It is drawn into a very thin wire (diameter 0.1 mm.). This wire is cleaned with 000 emery paper to remove any oxide layer present over the wire. This is made into rings (diameter 0.5 mm.). Two such rings are introduced in each of the eight turns of the filament.

Cleaning the substrates. — The success of metal deposition process depends mainly on the cleanliness of the surface of the substrate. Any films of grease on the surface cause the evaporated films to be soft and non-adherent. Moreover, grease and impurity films over the surface reduce the reflection
coefficients and increase the adsorption to a great extent, both of which are undesirable. Van den (51) states that a layer of grease 1 molecule thick is sufficient to affect the deposit. The following procedure is adopted for cleaning the substrates:

(a) The plates are treated in (con.) chromic acid for ten minutes.
(b) After the acid cools down, the plates are removed by a pair of tongs and washed with distilled water. This removes all the grease and impurity films. The criterion for this is that water clings to the surface in a continuous film. To avoid any further contamination the plates are kept under distilled water.
(c) The plates are dried with linen towel. Proper care is taken in the washing, storing and handling of the towels.
(d) Further, the plates are again cleaned in alcohol which removes a layer of organic matter which may be present on them. They are again dried by another towel of linen.
(e) In spite of all these precautions, it is impossible to have the surface completely free from films of grease. If however, these films are sufficiently thin they can be removed by bombardment with positive ions. This is done by passing a high tension discharge through the bell jar for ten minutes at a pressure of 0.01 mms.
(B) EXPERIMENTAL TECHNIQUE FOR EVAPORATION PROCESS

The process is dependent upon the fact that molecules are released from the mass of the metal if its temperature is raised to a point where its vapour pressure is greater than the pressure surrounding it.

When the substrates are cleaned they are mounted in their supports over the filament and the bell jar is lowered over the ring gasket which is greased properly by high vacuum grease (Dow Corning & Co.) useful at pressures of at least $10^{-6}$ mms. The backing pump is then started and the valve C2 is opened and pumping is continued until the pressure is reduced to 0.1 mm., when the H.T. discharge and the diffusion pump are switched on. The discharge not only removes the grease films but releases gases adsorbed on the surfaces of the glass and metal parts inside the chamber.

After about 15 minutes, the diffusion pump reduces the pressure below the limit of the backing pump and when the pressure reaches $10^{-3}$ mms. the vacuum becomes non-conducting and the discharge disappears. Pumping is continued for another five minutes to obtain a further reduction in pressure. Apiezon oil 'B' (vapour pressure $10^{-6}$ mms.) is used in the diffusion pump. Since an ionisation gauge is not used, the exact vacuum attained is not known except that it is always $10^{-5}$ mm. or better as read on Pirani gauge. However, the rate of degassing of the apparatus is frequently measured and is
found to be quite low. The evaporation is now carried out by switching on the variac and passing a current of about 5 amps. through the filament. The copper rings melt and cling to the filament. Sometimes spurtting occurs and the dissolved gases inside copper metal are given out. This causes the molten metal to grow in size and burst. This is avoided by slow heating of the filament. When this ceases and when some initial charge is evaporated for a few minutes, the shutter is opened for a known time. the desired 

After deposition takes place as required, the filament and supply to the diffusion pump are switched off. The diffusion pump continues to work for a short period and the vacuum gauge is watched until a slight rise in pressure is indicated. This shows that pumping has ceased and the valves C1 and C2 are closed to isolate the backing pump from the remainder of the system. When the diffusion pump is cooled down, the air inlet valve L is opened, the filmed quartz is removed for reflection and transmission measurements, and the system is closed with the bell jar.

The following precautions are observed:

(1) High standard of cleanliness is maintained throughout. A minute speck of foreign material is, under low pressure conditions, capable of producing several thousand times its volume of vapour. If any dust and cotton particles are seen through a magnifying lens, they are removed.
(2) Hands are always washed with soap, when any part inside
the chamber is to be handled.

(3) A steady supply of tap-water is passed to cool the
diffusion pump.

(4) The bell jar and the system is cleaned with linen
pieces, soaked in benzene, before evaporation is started.

(5) Any sputtering during H.T. discharge is reduced by
using aluminium heads for the probes. If the system is
clean, unwanted films do not appear over the substrate
during discharge.

(6) The initial and final charge of copper is always
avoided for deposition on quartz. Initial charge
contains oxide of copper as well as traces of impurities
having low melting points.

(7) The rate of deposition is near about \(2 \text{\ A/sec.} \) for all
the films under investigation.

Givens\(^{(29)}\) states that the vacuum condition during
evaporation are very important, for copper at least. He reports
that pressures should be less than \(10^{-5} \text{ mms.} \) if good copper films
free from cuprous oxide are to be obtained. The opaque copper
films oxidises surprisingly slowly upon exposure to air. This is
found to be so by resistance measurements in the present
investigation. It is shown by White and Germer\(^{(52)}\) that a
single crystal of pure copper oxidises to a depth of only \(25 \text{\ A} \) in
twenty four hours and a limiting oxide layer of about \(50 \text{\ A} \) forms
after years of exposure.

(C) **GENERAL FEATURES OF THIN FILMS**

As metal is deposited on a substrate it does not immediately form a continuous sheet. The first atoms to land, migrate over the surface, some perhaps escape from the surface, some come to rest. The existence of surface motion of the condensing atoms is confirmed by electron diffraction observations on very thin layers by Germer (53). Those atoms that come to rest serve as nuclei for new comers. The orientation of these atoms is due to the combined effects of forces of temperature orientation and the attractive forces of the Van Der Waals type. It, therefore, and the physical condition depends upon the nature of the substrate. Condensation on heated monocristalline substrate may yield films which are themselves crystalline, the process being called epitaxy. The new coming atoms which strike such a nucleus come to rest, enlarging the nucleus. This means that the surface layer must grow in patches which eventually coalesce as more material is added. This aggregation depends not only on the metal, the substrate and the temperature, but also on the rate of deposition of the films. Sennett and Scott (54) have shown from electron micrograph studies, that slower the rate of deposition, greater is the aggregation, and hence increased light absorption.

Since these patches increase in thickness as well as in area,
one may have considerable material on the surface before electrical continuity is established.

Just how much material is on the surface when continuity starts depends upon several factors.

Avery (55) concludes from researches on metallic films obtained by different methods that films produced by evaporation resemble the massive metal more closely than films produced by electrolytic deposition or cathodic sputtering. Halliday, Aymer and Wright (56) have examined thin films of copper prepared by vacuum evaporation, by electron diffraction method. They report that Cu specimens consist of crystallites in the form of discs (diameter $\approx 90\AA$ and thickness $\approx 15\AA$) parallel to 111 plane. Electron micrographs showed that the structure of copper films thinner than 200 $\AA$, was aggregated (Sennett and Scott (54)). The aggregation did not appear as regular and as well defined as in silver and gold films.

The light transmitted by copper films 200 $\AA$ thick, shows a maximum transmission band between 5700 $\AA$ to 5800 $\AA$. Thus there appear to be two main factors, apart from the obvious conditions such as purity of the material and cleanliness of the substrate, which influence the structure and therefore the optical and electrical properties of evaporated films: 1) residual gas pressure and ii) rate of deposition. It has been found that to obtain metal films of low optical absorption, low pressure
and high rates of deposition are required. The results of requirements Burridge, Kuhn and Perry (57) for aluminium confirm this notion. Even at $10^{-5}$ mms. and at fairly high rates of deposition, $10^3$ Å/sec. the number of gas molecules striking the substrate per second is of the same order as the number of metal atoms. Of course, most of the gas atoms bounce off, whereas most of the metal atoms stick. Mostovetch (58) working with an all glass system reported marked differences in the electrical resistivity of films evaporated at a pressure of $10^{-6}$ mms. as compared to $10^{-7}$ mms. Recently Aziz and Scott (59) have reported an effect of incident atomic velocity on the structure of evaporated silver films. Holland (60) found that aluminium films formed at $80^\circ$ incidence have a greater absorption than those condensed at normal incidence and develop a diffuse reflecting surface before becoming opaque.

II. ELLIPSMETER

The main features of the ellipsometer or polarization spectrometer used for determining refractive index $n$, absorption index $k$, are summarised below:

(A) SPECTROMETER ASSEMBLY:

Spectrometer assembly, consisting of the following components:

(1) A powerful source of light giving a continuous spectrum,
a compound lens for obtaining a high degree of
collimation and interference filters of minimal band-
widths.

(2) A spectrometer with collimator and telescope arms
swinging in a horizontal plane and having a scale on
a large fixed circle having a least count of 1'.

(3) A polariser mounted in a circular calibrated holder,
which is fixed in the telescope arm.

(4) An analyser and a quarter-wave plate mounted in a
similar way on the collimator arm.

(B) QUARTER WAVE COMPENSATORS:

Construction and calibration for the wave lengths of
the interference filters used.

(C) PHOTOMULTIPLIER TUBE ATTACHMENT:

Photomultiplier tube with its attachment and a stabiliser:
Construction of equipment and checking the stabiliser for voltage
regulation. This is used for determining the extinction
positions to a high degree of accuracy.

(D) WORKING OF THE ELLIPSOMETER
ELLIPSOMETER

WITH PHOTOMULTIPLIER TUBE ATTACHMENT AND

VOLTAGE STABILISER
(A) SPECTROMETER ASSEMBLY:

An instrument on the lines of the above specifications is shown diagrammatically in Figure 2. This instrument is assembled by suitable modifications and mountings on an old spectrometer. After removing the collimator and the telescope, rectangular horizontal plates 30.8 cms. x 7.2 cms. x 1.26 cms. are firmly attached to the telescope and collimator arms of the spectrometer. These plates carry sliding carriers which can be fixed with the screw attachment and are used for mounting polariser, analyser and compensator. The longer plate (fixed to the telescope arm) carries the source Π, a tungsten lamp (6 volts, 36 watts). An aperture of 3 mm. is placed at the tungsten lamp. A compound lens L (focal length 16 cms.) collimated the beam of light to a high degree. Another circular slit S of 5 mm. diameter is interposed in the collimated beam. Interference filter I is kept between the polariser Π and slit S. Interference filters (supplied by Barr and Stroud, London) of wave lengths 630 m/λ, 546 m/λ and 435 m/λ with a band-width of ± 5 m/λ are selected. The polarizer is mounted in a rotating circular holder with a degree scale (diameter 13.5 cms.). The four faces of the polariser are coated black with aquadag to ensure high absorption of the ordinary beam. It is fixed up in a cylindrical cork piece which is mounted in a metal cylinder. The polarizing nicol is so placed that when viewed directly through the eyepiece (without analyser), there is no lateral shift of the image of
the circular slit with respect to the cross wire, when the polariser is rotated. This ensured that the axis of symmetry of the polariser coincides with the axis of rotation of the circular scale. The inside surface of the hollow cylinder is also coated with aquadag to reduce any multiple reflections of the scattered light. The whole arm carrying source, collimating lens, slit, interference filter and polarizer is capable of rotation in a horizontal plane. Again, in order that this arm should not bend and should rotate smoothly without friction, a vertical rod is attached below to work as a support. The bottom of this supporting rod is fixed to a bearing having a single ball. The whole weight of the arm is thus carried by the ball, which rolls over a smooth glass surface fitted on the table for this purpose. On the other steel plate are mounted a $\lambda/4$ compensator $\mathcal{C}$, and analyser $A$, eyepiece $E$ and the photomultiplier tube $\mathcal{H}$. The compensator $\mathcal{C}$ is mounted vertically, in a rotating circular scale (diameter 8 cms.) having a least count of 5'. The analysing nicol is mounted in a similar way as the polarising nicol, except that its circular scale (diameter 14.8 cms.) is attached with a vernier (least count 0.01°) and a slow motion screw. The light is diaphragmed down to an aperture of 3 mms. at the analyser. This value of the aperture is found by trials. It was observed that the scattered light entering the analyser from outside has an observable effect on the extinction positions of the $\lambda/4$ plate and analyser. Therefore this was very necessary.
The eyepiece focusses the light on the photo cathode. The photomultiplier is enclosed in a suitable aluminium box so as to shield it completely. The box is painted with aquadag both from inside and outside, and is connected to earth. The output of the photomultiplier is given to the multiflex galvanometer through shielded wires.

The light polarised at an azimuth of 45° is allowed to be incident on the film $F$ and the reflected elliptically polarised light is analysed by the method outlined in (D) described on page 34.

(B) QUARTER WAVE COMPENSATORS:

CONSTRUCTION AND CALIBRATION OF $\frac{\lambda}{4}$ COMPENSATORS:

The $\frac{\lambda}{4}$ compensator is one of the most sensitive compensators (sensitivity $5 \times 10^{-5} \times 2\pi \lambda$). An excellent exposition on the relative merits of different types of optical compensators is given by Jerrard (61). The analysis of elliptical polarisation with the help of these compensators is fully discussed by Richartz and Hsien Yu Hsu (62), Hartmann (63) and Bruhat and Grivet (64). To attain the highest accuracy, it is necessary that the compensator plate is exactly a $\frac{\lambda}{4}$ plate for the wavelength used. This construction is a very tedious one and is complicated by the reflections that
occur at the boundary faces. The details about this are fully discussed by Rabinowitch and Cotton (65). These reflections have the effect of reducing the phase difference, because of the plate alone and making the plate act as if it were dichroic. This effect was taken into account in constructing and calibrating the plates.

The following construction procedure as outlined by Emberson (65A) was followed. Mica is very suitable for preparing such plates, since it can be cleaved to thicknesses of \((15 \times 10^{-5})\) cms. with surfaces of high natural polish and uniform to 20 \(\AA\). In this procedure, Indian Ruby mica is used. When multiple reflections are ignored, the phase difference \(\Delta\), produced between the two components along the fast and slow directions of the plate, is given by

\[
\Delta = 2 \pi \left( \frac{1}{\lambda_f} - \frac{1}{\lambda_s} \right) \frac{t}{\lambda}
\]

After substituting the values for \(\frac{1}{\lambda_f}\) and \(\frac{1}{\lambda_s}\) for mica from International Critical Tables and for the wave lengths chosen 630 \(\mu\)\(\lambda\), 546 \(\mu\)\(\lambda\) and 435 \(\mu\)\(\lambda\), the thicknesses \(t\) obtained for producing a phase difference \(\Delta = \frac{\pi}{2}\) are given in the following table:

<table>
<thead>
<tr>
<th>Wave length m(\mu)(\lambda)</th>
<th>Thickness mms.</th>
</tr>
</thead>
<tbody>
<tr>
<td>630</td>
<td>0.035</td>
</tr>
<tr>
<td>546</td>
<td>0.030</td>
</tr>
<tr>
<td>435</td>
<td>0.023</td>
</tr>
</tbody>
</table>
A mica plate initially of thickness 0.25 mms. is cleaved under water by a procedure given by Benedick (66). After cleavage, the thicknesses are measured by a micrometer screw (least count 0.005 mms.) and the plates with uniform thicknesses for appropriate wave lengths are sorted out, and labelled R, G and V. The plates of thicknesses less than required are thrown off while plates with thicknesses greater than required are further cleaved. About 100 such plates of approximate thicknesses for each wave length were selected. Every plate from this stock is further tested by means of a Babinet Compensator, for the final selection of a plate with a phase difference \( \Delta = \pi/2 \) approximately for each wave length. This is done in order to check the approximate thicknesses found by the theoretical formula. Each of the above approximate \( \lambda/4 \) plate is mounted for calibration by a procedure adopted by Jerrard (67). Out of the 100 plates, 10 best plates are selected for each wave length by preliminary calibration. Each of the 10 plates for each wave length is embedded in Canada Balsam on an annealed cover glass, so as to suppress multiple reflections.

Of these ten plates for a single wave length, the best one is selected by final calibration by the same method. Results of calibration are given below for each of the best \( \lambda/4 \) plates for the given wave length.

In short, the procedure for calibration is as follows:
A parallel beam of light is passed through a polariser, a mica
plate of arbitrary thickness (Plate 1: preferably not a $\lambda/4$ plate), the plate under test (Plate 2: approximate $\lambda/4$ plate) acting as a compensator and the analyser. All the components are mounted so that they can rotate about the same axis. The plate 2 and analyser have graduated circles having least count of 5 minutes. The light is diaphragmed down to an aperture of about 3 mms. at the analyser. Initially the polariser and analyser are crossed and plates 1 and 2 are set so that the field of view is dark. Plate 1 is rotated through $10^\circ$ so that an elliptically polarised light falls on plate 2. Plate 2 and the analyser are rotated until a dark field of view is obtained. The analyser reading (a) and compensator reading (b) are noted. The same components are then rotated until a second extinction position is obtained. The circle readings A and B are again noted. Then the phase difference $\Delta$ is found from the equation

$$\cos \Delta = \frac{\tan (A - a)}{\tan (B - b)}$$

The procedure is repeated for different positions of plate 1 and a mean value for $\Delta$ was obtained.

<table>
<thead>
<tr>
<th>Wave length $\mu\mu m$</th>
<th>Phase difference $\Delta$ for best $\lambda/4$ plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>630</td>
<td>$89^\circ 42' \pm 0^\circ 2.5'$</td>
</tr>
<tr>
<td>541</td>
<td>$89^\circ 46' \pm 0^\circ 3.2'$</td>
</tr>
<tr>
<td>435</td>
<td>$80^\circ 15' \pm 0^\circ 2.0'$</td>
</tr>
</tbody>
</table>
The probable error of observation was calculated by Peter's formula:

\[ e = 0.8453 \frac{\sum f}{n} \]

where \( n \) = number of observations \( f \) = residual.

After the three best plates are selected, they are mounted on a cardboard and the direction corresponding to the fast axis is marked on it as determined by a procedure outlined by Wood.

Typical calibration readings for the best \( \lambda/4 \) plate corresponding to wave length 630 m/\( \lambda \) are given in the following table.
<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Scale reading of Plate I</th>
<th>Analyser Scale</th>
<th>Scale reading of ( \lambda/4 ) Test Plate</th>
<th>( A-a )</th>
<th>( B-b )</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>10°</td>
<td>63° 24'</td>
<td>47° 18' 214° 124° 48°</td>
<td>16° 6'</td>
<td>89° 12'</td>
<td>89° 52'</td>
</tr>
<tr>
<td>2.</td>
<td>20°</td>
<td>78° 39° 15'</td>
<td>39° 48° 207° 12° 116°</td>
<td>38° 45'</td>
<td>89° 12'</td>
<td>89° 52'</td>
</tr>
<tr>
<td>3.</td>
<td>30°</td>
<td>68° 18' 24°</td>
<td>34° 12° 207° 12° 116°</td>
<td>43° 54'</td>
<td>91° 13'</td>
<td>91° 10'</td>
</tr>
<tr>
<td>4.</td>
<td>40°</td>
<td>87° 54° 19°</td>
<td>19° 3° 213° 36° 123° 48°</td>
<td>69° 51'</td>
<td>89° 48'</td>
<td>89° 22'</td>
</tr>
<tr>
<td>5.</td>
<td>50°</td>
<td>70° 45° 4°</td>
<td>15° 229° 54° 140°</td>
<td>66° 20'</td>
<td>89° 48'</td>
<td>89° 40'</td>
</tr>
<tr>
<td>6.</td>
<td>60°</td>
<td>61° 33° 4°</td>
<td>59° 234° 6° 144° 26°</td>
<td>56° 34'</td>
<td>89° 30'</td>
<td>89° 24'</td>
</tr>
<tr>
<td>7.</td>
<td>70°</td>
<td>53° 33° 15°</td>
<td>28° 224° 12° 144° 6°</td>
<td>38° 5'</td>
<td>90° 6'</td>
<td>90° 44'</td>
</tr>
<tr>
<td>8.</td>
<td>80°</td>
<td>51° 24°</td>
<td>34° 9° 226° 34° 135° 24°</td>
<td>17° 15'</td>
<td>91° 6'</td>
<td>91° 20'</td>
</tr>
</tbody>
</table>

Mean \( \Delta = 89° 49' \)
In the last twenty years, attempts have been made to substitute the eye by the photo cell. This is not only desirable to relieve eye strain, but also particularly useful in the ultra violet and near infra-red portions of the spectrum. Bruhat and Guinier (68) seem to be pioneers in this field. Bor (69) employed a photo cell connected to a Lindemann electrometer to determine the correct extinction positions. An interesting variation is that due to Kent and Lawson (70) whose scheme consists in converting the elliptically polarised light into a circularly polarised light by means of a fixed phase plate of mica. This circularly polarised light is passed through a revolving nicol prism (40 r.p.s.) and is then incident on a photo cell.

An ingenious photographic method, enabling measurements to be made simultaneously at several wave lengths, has been described by Bor (71). Among the most recent photo-electric methods, with which azimuth and phase difference determinations may be made with an accuracy of 2 minutes of arc, is that given by Archard, Clegg and Taylor (72). Rothen (73) has obtained an accuracy of the same order with the ellipsometer using a $\lambda/4$ plate and a half-shade system.

An accuracy of the same order is obtained in the present method by the use of photomultiplier tube for determining the correct extinction position. The photo-multiplier tube, type
931A with the following specifications, was used in the circuit diagram as shown in Figure 3.

- Sensitivity = 9300 \( \frac{\text{amps.}}{\text{watt}} \)
- Anode supply = 1250 volts, D.C.
- Anode current = 1.0 mA
- Anode dissipation = 0.25 watts
- Ambient temperature = 75\(^\circ\) C.
- Luminous sensitivity = 10 amp. per Lumen
- Current amplification = 10\(^6\)

The employment of photomultiplier for the measurement of low light levels has been studied in some detail by Engstrom (74). Since these tubes are particularly suitable for the measurement of extremely small quantities of light, extinction position can be judged with a high degree of accuracy.

Also the degree of amplification is very sensitive to changes in the overall voltage. The rectifier which supplies this voltage is stabilised in such a manner as to eliminate effectively any fluctuations. An electronically stabilised power supply is constructed in the laboratory. Its output varies only \( \pm 0.1\% \) for mains voltage variation of \( \pm 1.0\% \). A good discussion of design procedure involved in a voltage regulated power supply illustrated in the figure is given by Bereskin (75).

Here a neon tube (N.T.) is used as a gaseous voltage regulator which produces a constant potential that is used for reference purposes. It also maintains the cathode potential of
a valve (6SJ7) at a fixed potential irrespective of the input voltage $E_s$ applied to the regulator system. The valve (6SJ7) is a sharp cutoff pentode and is operated as a direct-coupled amplifier, the output of which is applied to the control grid of valve (6L6). This tube acts as a variable load. Since the transconductance ($g_m$) is controlled by the grid voltage, it ($g_m$) is changed in such a manner that any change in plate voltage of valve (6L6) is compensated by a corresponding change in the grid voltage.

The regulated voltage is fed to a D.C. voltmeter (0-10 volts. : 1000 ohms. per volt.) which is converted to read up to 1000 volts. by suitable arrangement of resistances. By the adjustment of the potentiometer, stabilised voltages ranging from 500 volts. to 900 volts. are available. Thus maximum voltage of 100 volts. can be suitably applied between the dynodes of the photomultiplier.

The output of the photomultiplier tube was fed to a multiflex galvanometer having a current sensitivity of $(2 \times 10^{-9})$ amps. per mm., and an internal resistance of 4600 ohms. This galvanometer is very useful for finding extinction positions, since the sensitivity is increased in three steps $2 \times 10^{-7}$ amps./mm., $2 \times 10^{-8}$ amps./mm. and $2 \times 10^{-9}$ amps./mm. Rough adjustments of extinction positions are made with lower sensitivity. Finer adjustments are made with the highest sensitivity.
The following precautions are observed:

(1) The photomultiplier tube is enclosed in a suitable aluminium box. The box is painted with aquadag both from inside and outside, and is connected to earth so as to shield it completely from stray light and electrical disturbances.

(2) Shielded wires are used for connecting the photomultiplier to the multiflex galvanometer. The outside shield is earthed.

(3) Operation of the photomultiplier is not carried out above 1 milliampere, because of excessive fatigue. For most stable operations light flux, producing currents over 100 microamperes, is never allowed to be incident on the photo cathode. Initial adjustments of the extinction positions are always made by the eye.

(4) The positive terminal of the regulated power supply is connected to earth.

(5) The chasis along with the metal casing of the power supply is also connected to earth.

(6) All observations were carried out after 15 minutes after the stabiliser is switched on, so that a steady condition of the working of the circuit is attained.

(7) The regulation of the power supply is checked from time to time.

(8) All observations are taken in a dark room.
(9) A suitable shutter is interposed so as to cut off light beam falling on cathode, when readings are not taken.

(D) WORKING OF THE ELLIPSMETER:

Before using the ellipsometer preliminary adjustments are made as follows:—

(1) The metal tubes holding the analyser, polariser and the quarter plate are made horizontal by means of a spirit level bottle. This is done by means of adjustable screws fixed to the vertical stand supporting the tubes.

(2) Preliminary orientations of the nicols are accomplished by the Wollaston prism. The optic axis of the polariser P is set at an azimuth of 45°.

(3) The filmed quartz plate is mounted vertically by a special mount on the prism table which is levelled.

(4) The centre of the cross wire is exactly at the centre of the reflected image.

(5) All the measurements are made at one angle of incidence (70°) which is near about the angle of principal incidence for the three wave lengths chosen for copper. The ellipticity is greatest for this angle of incidence for which phase difference between the P and S components \( \Delta = \Delta_p - \Delta_s = \frac{\pi}{2} \). Drude (4)
has shown that errors of measurement are least when observations are made at an angle of incidence for which 
\[ \Delta \approx \frac{\pi}{2}. \]

(6) For semitransparent copper films which are used in these investigations, it is necessary to reduce the out of phase reflection from the other surface of quartz. This could be done by coating the back surface by aquadag, but since the same quartz plate is used for transmission measurements, the back-reflection is effectively reduced by keeping a black paper (used for keeping X-ray films) behind the quartz plate.

(7) Complete extinction could never be obtained by the combined adjustment of the compensator and analyser but only a minimum intensity as seen on the scale of galvanometer.

(8) Pure copper is reported to have an absorption band with its long wave length limit between \( \lambda = 5500 \) Å and \( \lambda = 6000 \) Å. Therefore, interference filters having a range \( \lambda = 4350 \) Å to \( \lambda = 6300 \) Å were selected.

The principal experimental facts are summarised as follows:

(1) Absorbing films do not completely polarized light at any angle of reflection.

(2) Plane polarised light is, upon reflection changed to elliptically polarised light, unless the plane of vibration is either parallel or perpendicular to the
VIBRATION ELLIPSE

Figure 4
plane of incidence.

(3) The ellipticity is due to a phase difference $\Delta$ between the $p$ and $s$ components. At an angle of principal incidence $\phi$, $\Delta = \pi/2$.

(4) Circularly polarised light incident at an angle $\phi$ is reflected as plane polarised light with its plane of vibration making an angle $\gamma$ with the plane of incidence. This angle is the angle of principal azimuth.

The optical constants $n$ and $k$ of the copper film are determined by analysing the reflected elliptically polarised light (Figure 3).

Hartmann (63) has outlined a method for determining the ratio of the complex reflection coefficients. It is defined by two parameters

$$\int e^{i\Delta} = \frac{R'p}{R's}$$

while the polarising assembly has four parameters. They are the azimuths of the polariser and analyser, azimuth of the slow axis of the and the phase difference of the compensator plate compensatory. Such a polarising assembly as is used in this experiment can be solved by a matrix equation outlined by Jones (76). Richartz and Hsien Yu Hsu (62) have fully explained the methods for the analysis of elliptically polarised light.

When two coherent waves having respective amplitudes $a_1$ and
a_2 are vibrating at right angles to each other with a phase difference \( \Delta \), their resultant is elliptically polarized light. The semiaxes of the ellipse are designated \( A \) and \( B \) respectively. The inclination of the \( A \) axis with respect to \( a_1 \) is denoted by \( \gamma \). The angles \( \psi \) and \( \nu \) are defined by equations (Fig 4)

\[
\tan \psi = \frac{a_1}{a_2} \quad \ldots \ldots \ldots \ldots \ (1)
\]

\[
\tan \nu = \frac{B}{A} \quad \ldots \ldots \ldots \ldots \ (2)
\]

\( \psi \) and \( \Delta \) are determined from the measurements of \( \gamma \) and \( \nu \) with a \( \lambda/4 \) compensator and analyser. The procedure is outlined in any standard text book of light (Wood, Monk Jenkins and White). From the values of \( \psi \) and \( \nu \), the relative amplitudes and phase difference of the original components are calculated from the following formulae (Schuster 77).

\[
\cos 2 \psi = \cos 2 \nu \cos 2 \gamma \quad \ldots \ldots \ldots \ldots \ (3)
\]

\[
\tan \Delta = \frac{\tan 2 \nu}{\sin 2 \gamma} \quad \ldots \ldots \ldots \ldots \ (4)
\]

From the knowledge of the angle of incidence \( \phi \), angle of azimuth \( \psi \) and the phase difference \( \Delta \), the constants \( n \) and \( k \) are computed from the following formulae:
\[ F = n^2 - k^2 \]

\[ = \sin^2 \phi + \frac{\sin^2 \phi \tan^2 \phi (\cos^2 \gamma - \sin^2 \gamma \sin^2 \alpha)}{(1 + \sin^2 \gamma \cos \alpha)^2} \]  

(5)

\[ G = 2nk \]

\[ = \frac{\sin^2 \phi \tan^2 \phi \sin 4 \gamma \sin \alpha}{(1 + \sin^2 \gamma \cos \alpha)^2} \]  

(6)

\[ h^2 = (n^2 + k^2)^2 \]

\[ = F^2 + G^2 \]  

(7)

\[ n^2 = \frac{H + F}{2} \]  

(8)

\[ k^2 = \frac{H - F}{2} \]  

(9)

III. A UNICAM SPECTROPHOTOMETER

FOR THE MEASUREMENT OF PERCENTAGE TRANSMISSION:

A unicam S.P. 500 spectrophotometer is used for transmission measurements from 200 m\(\mu\) to 1000 m\(\mu\). The following are some of the salient features:

(i) The resolving power is of a very high order and is maintained in the ultra violet
UNICAM SPECTROPHOTOMETER
(ii) The narrow band-width reduces to a minimum the effects of spectral impurity at the selected wave length.

(iii) Dark current is exceptionally stable, thus reducing the necessity for check readings.

(iv) The degree of reproducibility of observations is unusually high, — of the order of 0'2 per cent.

The sensitivity check and wave length check as outlined in the Unicam Manual are performed before the observations are carried out. Humid conditions inside the spectrophotometer are avoided by inspecting silica gel regularly and changing when necessary. It is particularly important to keep the photocell compartment free from moisture, if reproducible results are to be obtained.

It must be stressed here that all the necessary precautions given in the Unicam Service Manual are strictly followed. Moreover in all observations :

(1) The copper film surface is always on the incident side of the light beam. It is observed that when the uncoated side of quartz is towards the incident beam, the percentage transmission is higher than when the coated surface is towards the incident beam. Harria, Beasley and Loeb (78) have derived theoretical formulae for transmission of radiation by thin absorbing films on thick non-absorbing backings, by the method of intensity addition.
(2) Copper films are always deposited on the same quartz surface. This surface is marked by a small letter for the purpose of identification. This procedure eliminated any small differences in transmissions arising from small differences in the structure of the two surfaces.

(3) The hexagonal quartz surface is worked optically flat to $\frac{\lambda}{5}$.

(4) The quartz is placed perpendicular to the light beam. This is attained by a special mount, which is fitted on the cell-table, in one position only.

(5) The quartz piece on which a copper film is deposited, is of sufficient thickness (0.2 cms.). Hence any unwanted interference phenomenon due to backing alone are avoided.

(6) All measurements are taken after about twenty minutes, current in the after switching on the apparatus, so that stable conditions are reached and no drift in the readings takes place.

(7) Transmissions through filmed quartz are taken with respect to another unfiled quartz, which is kept the same throughout the experiment. This is so chosen from amongst several quartz pieces, that it has the transmission characteristics, approaching those of filmed quartz in the unfiled condition. That it is so is shown by the following table:
<table>
<thead>
<tr>
<th>Wave length m/(\mu)</th>
<th>Ratio of transmissions of two quartz plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.98</td>
</tr>
<tr>
<td>300</td>
<td>1.00</td>
</tr>
<tr>
<td>400</td>
<td>1.00</td>
</tr>
<tr>
<td>500</td>
<td>1.00</td>
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<td>600</td>
<td>0.99</td>
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<td>700</td>
<td>1.01</td>
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<tr>
<td>800</td>
<td>0.99</td>
</tr>
<tr>
<td>900</td>
<td>1.01</td>
</tr>
<tr>
<td>1000</td>
<td>1.00</td>
</tr>
</tbody>
</table>

IV. KOHLRAUSCH BRIDGE FOR MEASURING ELECTRICAL CONDUCTIVITY

Electrical conductivity of the films is determined by measuring the resistance of the films by a Kohlrausch Universal Bridge (Pye & Co., Cambridge) with multiplying coils of values 0.1, 1, 10, 100, 1000, and 10000. The range of resistances that can be measured accurately with the bridge is from 0.0005 ohm. to 100,000 ohms. The balance point is detected by a galvanometer of sensitivity \(10^{-6}\) amperes/mm. (Leeds Northrup Co.). Before using the bridge for the determination of resistance of films, it was calibrated with respect to standard low and high resistance boxes (Pye & Co.). The calibration was found to be up to the...
Resistance of film is measured both inside and outside the chamber, and the growth rate of oxide film is studied. For this purpose, a rectangular glass plate (2.5 cms. x 1.6 cms.) is initially coated with a very thick film of silver on the two sides leaving the central position (1.8 cms. x 1.6 cms.) blank. This is obtained by placing a thin rectangular glass cover slip (1.8 x 1.8 cms. No. 1 thickness) over the central portion, and this cover slip was firmly fixed up by a small clip. Silver is chosen for two reasons. Tolansky (79) has given adequate evidence that silver film contours the surfaces accurately on which it is deposited. It is also resistant to oxidation so that a good contact with silver films on both the sides of the glass substrate can be made with strong paper clips. The edges of the clips are very well polished with 000 emery paper to establish good contact. The clips are thoroughly cleaned to remove any colour coating which might give out undesired vapours in the vacuum system. This method of establishing contacts proved to be excellent in all respects. A copper film is deposited on this substrate as well as on thick films of silver near the sharp edges of the clips on the two sides of the substrate. The resistance of copper film is measured only after one hour of deposition, inside vacuum. Thus the resistance is measured only when the film cools down to the room temperature. Afterwards, the stopcock is opened to air and changes in the resistances observed at an interval of
20 minutes up to the first three hours, increasing this interval later. It is necessary that the film should be allowed to oxidise in a moisture-free atmosphere; therefore, the stopcock \( C_1 \) is closed while \( C_2 \) is opened so that a free communication of the evaporation chamber with the \( P_2O_5 \) trap is established. The quartz piece is then removed from the evaporation chamber for reflection and transmission measurements and the chamber is again closed with the bell jar. Observations are carried out on the same film in air for about 16 hours when it is observed that the rate of oxidation is asymptotic. The filmed substrate was then removed and the length \( (L) \) and breadth \( (b) \) was measured by means of a microscope (P. T. I., London) of least count 0.002 cms. In all calculations means of several readings for lengths and breadths are taken. If \( \sigma \) is the resistance of the film of length \( L \), breadth \( b \) and thickness \( d \), then the electrical conductivity of the film is given by

\[
\sigma = \frac{L}{\alpha} \cdot \frac{1}{b \cdot d},
\]

\text{mho/cm.}

V. A MULTIPLE BEAM INTERFEROMETER

FOR THE MEASUREMENT OF THICKNESSES OF THIN FILMS

BY THE METHOD OF FIZEAU FRINGES

The method has been developed to a remarkable degree by Tolansky (79) for using the interference effects arising from
two silvered surfaces when brought into close proximity to form a wedge of small angle. The study of the contour of an approximately plane smooth surface by using optical interference is originally due to Fizeau (80). The fringes, arising from interference between the light beams reflected from the silvered glass on the two sides of the air wedge are known as Fizeau Fringes or the Fringes of Constant Thickness. At points along the wedge where the path difference between the two beams (allowing for the phase changes at the surfaces) is an integral number of wave lengths, bright fringes are seen; where the path difference is an odd number of wave lengths, dark fringes occur. If a part of one of the plates is covered by a film (the thickness of which is to be measured) preferably with one edge lying parallel to the line of greatest slope of the wedge, the fringes are displaced on crossing the film edge. The thickness of the film is found from the displacement of the fringes. A typical interferogram shows the fringe displacement for thickness 380 Å.
The conditions for obtaining sharp Fizeau fringes are examined by Tolansky and Brossel (81). They are

(1) The surfaces must be coated with highly reflecting film of minimal absorption.
(2) This film must contour the surface exactly and be highly uniform in thickness.
(3) Monochromatic light must be used.
(4) The interfering surfaces must be separated by, at the most, a few wave-lengths of light.
(5) A well collimated beam (within 3° tolerance) must be used.
(6) The incidence should preferably be normal.

By consideration of the Uncertainty principle, Ingelstam (82) shows that the accuracy of measurement on a single fringe step is limited to \[ \frac{\lambda}{1000} \] i.e., \( 5.4 \AA \) for \( \lambda = 5461 \AA \).

Heavens (83) has obtained an accuracy of \( 5 \AA \) for a film thickness determined from a single step measurement and a correspondingly lower figure for the mean of several steps.

In this method to be outlined below, reflection fringes were used, the surface bearing the film being covered by an opaque layer of silver. This was to ensure that the reflection conditions above the film and above the unfilmed surface are the same. With these Fizeau fringes, very small thicknesses (below 50 Å) are very difficult to measure, since the
INTERFEROMETER FOR THICKNESS MEASUREMENT

Figure 5.

M = Microscope.
I = Interferometer plates.
F = Interference filter.
C1 = Condensing lens.
C2 = Collimating lens.
P = Pinhole.
S = Source: Mercury vapour lamp.

ABC = Flat glass surface.
AB = Copper film.
PQRS = Opaque silver film.
DE = Semitransparent silver film on optical flat.
displacement is very small. By using fringes of equal chromatic order or FEGO fringes, Scott, McLauchlan and Sennett (84) have measured thicknesses down to 15 Å with an accuracy of ± 5 Å.

The following experimental procedure is adopted: (Fig. 5)

The copper film AB is deposited on part of an optical flat, worked to \( \lambda/5 \). A fairly thick (opaque) coating of silver PQRS is then deposited over the flat. Tolansky (81) has given adequate evidence that silver fulfills the necessary conditions both in its high reflectivity and its ability to contour the surface. Weaver and Benjamin (85) have shown that this overlayer of silver should be greater than 500 Å in thickness. Otherwise the phase change at reflection shown to occur by Schulz and Scheibner (86) when a beam of light strikes the metal film at normal incidence, produces discrepancy in the thickness measurement. The height QR then equals that of the copper film AB. Another optical flat worked to \( \lambda/40 \) (Leitz Wetzler) having diameter of 4.5 cms. and thickness 1.5 cms. is also coated with a silver film DE, possessing an observable transmission. When this is brought near to AC and illuminated from above, back reflected Fizeau fringes are formed. They consist of very fine dark lines against a bright background. The step displacement RQ is thus determined with a precision down to 10 Å. By this method the true metrical thickness is obtained.

A jig is constructed for holding the interferometer plates,
and for obtaining a suitable wedge. It consists of two ebonite discs of equal size, having a diameter 7·5 cms. To one of these discs, which supports the glass plate ABC, three screws, each 4 cms. in length are fixed up vertically forming equilateral \( \triangle \) with a side 5·5 cms. A steel spring of length 1·5 cms. is placed over each of these screws. The optical flat DE is held firmly by means of other ebonite disc. A concentric disc of radius 3 cms. is removed from this piece in order to view the fringes. Three small holes are bored to this disc to pass the screws. This disc together with the optical flat is made to rest on the springs. Three nuts are then fitted at the top of the screws. The distance as well as the wedge angle could be suitably adjusted by such an arrangement.

A low power ( x 50 ) microscope ( P. T. I., London ) having a least count 0·002 cms. is used for observing the fringes. A working distance of 2·5 cms. could be conveniently obtained. Mercury vapour lamp is used as the source. A high degree of collimation is attained by the use of condenser, collimator and a pin hole. An interference filter ( green 5461 Å) is placed in a collimated beam.

The fringe width ( equal to \( \lambda/2 \) ) and the fringe displacement are measured and the thickness found out simply by the rule of three. A mean of several steps is then found out. That the film thickness determined this way is of the correct order of magnitude was roughly checked by the following methods.
in the case of a single film:

(1) Method of weighing the film on a micro-balance, assuming the density of the film to be equal to the density of the bulk metal.

(2) Polarimetric method outlined by Emerson (87) gave a complex quantity for the thickness, the real part of which was of the same order as that determined above.

(3) Method of transmission measurements, neglecting the multiple reflections within the film, and taking the value of $nk$ as determined by reflection measurements.