CHAPTER 2
EXPERIMENTAL DETAILS

(A) FABRICATION OF CVD SYSTEM AND PREPARATION OF HOMOGENEOUS AND GRADED-INDEX ALUMINIUM OXIDE THIN FILMS.

(B) OPTICAL MEASUREMENTS AND CHARACTERIZATION OF HOMOGENEOUS AND GRADED-INDEX ALUMINIUM OXIDE THIN FILMS.

2.1 Introduction

Section (A) starts with details of the fabricated CVD system. The experimental procedures for preparation of homogeneous aluminium oxide films are then given using this technique. A novel 'MOCVD process' developed for the preparation of graded-index thin films is then described.

In section (B), experimental details for the measurement techniques like ellipsometry and spectrophotometry are given, along with their measurement procedures. The analysis procedures for the determination of optical constants of homogeneous and graded-index thin films, as followed from literature, are given in this chapter.

The characterization of homogeneous and graded-index thin films have been performed by using ESCA, the experimental details of which are given in section (B).

However, the improved methods in the analysis and characterization of non-absorbing graded-index thin films developed during the course of the present work are described in chapter 5.
2.2 Fabrication details of CVD system

This section covers fabrication details and specifications of the Chemical Vapour Deposition system fabricated by the author. It was planned to fabricate a general purpose CVD system for the deposition of various dielectric thin films to suit various requirements of the laboratory. The system can be used to deposit various thin films within the limitations mentioned below.

The design is based on the horizontal displacement flow reactor system which is most suited for laboratory work and sometimes also in industries for small scale use. With this reactor, chemical processes like pyrolysis, reduction, oxidation, hydrolysis, nitride and carbide formation can be carried out for thin film deposition, at atmospheric pressure.

The schematic diagram of the CVD system, fabricated, is shown in Fig. 2-1. The photograph of the resistively heated CVD system along with the induction heater is shown in Fig. 2-2. The photograph of the CVD system, specifically, with induction heater is shown in Figure 2-3. The schematic diagram of experimental MOCVD set up is shown in Figure 2-4.

The fabrication details of the CVD system are given below unitwise for (1) gas controlling and purification units (2) flowmeter panel (3) bubbler units (4) inlet and outlet units and (5) chemical reactor units.
FIG. 2-1: Schematic diagram of general purpose CVD system.
FIG. 2-2 CVD System with resistance furnace
FIG. 2-3 CVD System with induction heater
1. HEATER FOR BUDDLER, 2. REACTANT MATERIAL, 3. BUDDLER
4. INLET FOR CARRIER GAS, 5. THERMOMETER, 6. EXHAUST II FOR BY PASSING
7. INLET FOR DILUENT GAS, 8. HEATING CARD, 9. SUSCEPTOR OR HEATING PLATE
10. SUBSTRATES, 11. INDUCTION HEATER OR RESISTANCE FURNACE
12. INLET FOR INITIAL PUMPING, 13. WINDOW FOR PYROMETER OR THERMOCOUPLE
14. EXHAUST I FOR BY-PRODUCTS.

FIG. 2-4: SCHEMATIC DIAGRAM OF MOCVD SET-UP
2.2.1 Gas controlling and purification units

The gas controlling and purification units are incorporated for gases Ar, He, N\textsubscript{2}, H\textsubscript{2} and O\textsubscript{2}. High purity gases (IOLAR2 grade, 99.99\% purity, obtained from Indian Oxygen Ltd., Bombay) are used for the thin film deposition. To obtain controlled discharge of pressure, two stage regulators (Model 8, Matheson, USA) are used. For the filtration of particles larger than 0.3 microns Matheson's (Model 6184T44) filters are used at a stage before the gas purifier units. Even though high purity gases are used, different Matheson's gas purifier units have been incorporated for final stage gas purification. Removal of oil, water and foreign particles from the gases N\textsubscript{2}, H\textsubscript{2} and O\textsubscript{2}, is accomplished through the use of calcium aluminosilicate 13 x molecular sieve (Matheson, Model 450) purifier. To remove oxygen and water from the inert gases namely Ar and He, a gettering furnace (Matheson's model 8301 Hydrox purifier) is incorporated. For removing the oxygen from hydrogen gas, an oxygen removing purifier (Matheson's model 64-1010 purifier) is incorporated.

2.2.2 Flowmeter panel

Input gas flow rates are measured and controlled by rotameter type flowmeters coupled with precision needle valves. Matheson's rotameters (model 7642T) are assembled in the flowmeter panel with various tubes covering a total range of flow rates measurable from 0.04 to 49 l/min of air. The accuracy of the rotameter is typically \( \pm 5\% \) of the full scale reading. The outlet pressure is observed with 100 mm dial Bourdon type pressure meters (0-35 psi) after adjusting the rotameter needle valves. Teflon tubes, teflon valves and teflon
fittings (Nirmal Udyog, New Delhi), which can withstand working pressure up to 2.5 atm pressure, are used in the panel construction. The flowmeter panel can be used for various reaction processes mentioned above. The schematic diagram of flowmeter panel can be seen from the Figure 2-1.

2.2.3 Bubbler units

The source vapours can be generated either from a solid or liquid reactant material using a bubbler. The bubbler unit, shown in Figure 2-4, is fabricated with borosil glass (Borosil, Bombay) which can withstand up to 500°C (The dimensions of bubbler unit are: I.D., 5.6 cm; height, 10 cm). With this bubbler the reactant material can be by-passed to a separate exhaust without entering into the reaction chamber during pre or post deposition period. The exit of the bubbler unit is connected to the inlet unit through a ball and socket joint with a metal clip. A long stem thermometer is inserted in the bubbler to measure directly the temperature of the reactant material.

Two different bubbler heaters which operate at different temperature ranges are used. One is a constant temperature oil bath (liquid paraffin) for temperatures up to 180°C and the other is a beaker-shaped heating mantle for temperatures up to 350°C. The temperature of the reactant material can be measured and controlled, by thyristorised linear digital temperature controller (Model DTL/1, IEEC, Bombay). The temperature controller can be used up to 999°C and the calibration accuracy is ± 1% of full scale reading. The Chromel/Alumel thermocouple with stainless steel sheath material is used as a sensor for temperature measurement.
2.2.4 Inlet and outlet units

The inlet unit, between bubbler and reaction chamber, and the outlet unit, between reaction chamber and exhaust, are shown in Figure 2-4. Inlet assembly is used to mix the vapours generated from bubbler(s), reactant gas and diluent gas before their entry into the reaction chamber. These units are made of borosil glass. To avoid the condensation of reactant material on inside walls of the inlet unit, the inlet unit is maintained at nearly the same temperature as that of bubbler by winding it with a cord type heating mantle.

The outlet unit to the reaction chamber consist of three outlets. One outlet is to insert a thermocouple for measuring the substrate temperature in the case of resistance heating or act as a window for pyrometric temperature measurement in the case of induction heating. The second outlet is connected to the exhaust line directly without any external pumping. The third outlet is made to pump out the air by an oil-less vacuum pump before the entry of inert gases into the reaction chamber prior to film deposition.

2.2.5 Chemical reactor units

The horizontal displacement flow reactors are simpler in construction compared to other reactors. Two different tubes made of quartz and borosil glass are fabricated with identical dimensions (I.D., 5.6 cm; length, 60 cms). The choice of tube is made on the basis of deposition temperature. The substrate heating is carried out either by resistance heating or induction heating. Except the method of heating, the experimental set up for both kinds of heating is same.
as shown in Figure 2-4. The details of resistance and induction heating are given below.

2.2.5.1 Resistance heating

For resistance heating, a furnace is fabricated using a ceramic muffle (I.D., 6.4 cms; length 45 cms) wound with 2 kw nichrome tape. The length of the central hot zone is 28 cms. The maximum operating temperature is 800°. The temperature inside the furnace is measured and controlled by linear digital temperature controller (Conel, Poona). The calibration accuracy is ±1 % of full scale of 999°C. The temperature of the stainless steel plate (substrate holder) inside the reaction chamber is measured by chromel/alumel thermocouple (length : 60 cms) with stainless steel sheath material. The thermocouple is placed at one end of the St. steel plate through the outlet unit.

The silicon and borosilicate glass substrates are placed on a stainless steel plate (dimensions : 15 cms x 4 cms x 0.2 cm) as shown in Figure 2-5. The St. steel plate is placed on top of a rectangular borosil glass boat (15 cms x 4 cms and O.D., 0.6 cm.).

2.2.5.2 Induction heating

For induction heating, an induction heater (Type RF 3/W; Telecom Industries Pvt. Ltd., Bombay) with output power 6 KW and frequency 2 MHz is used with a horizontal RF coil as shown in Figure 2-3. The coil (I.D. 6 cms; length 23 cms; number of turns, 32; diameter of hollow copper tube, 0.635 cm) is made to suit the requirements for uniform heating throughout the susceptor. Two copper tubes are wound in parallel and one of the tubes is insulated with glass sleeve.
FIG. 2-5 Position of the substrates on susceptor and substrate holder
Silicon carbide coated graphite plate (Type PT 444, Ultra Carbon Corp., USA) is used as a susceptor (dimensions: 15 cms x 4 cms x 0.5 cm) for substrate heating. The silicon and borosilicate glass substrates are kept on a susceptor. The susceptor in turn is kept on top of fused silica stand (15 cms x 4 cms and O.D., 0.4 cm) as shown in Fig. 2-5. The susceptor temperature can be varied by the variac control manually. The maximum temperature that can be attained with this system is 1200°C, for higher temperature (> 600°C) substrate heating quartz tube is used. The susceptor temperature is measured by two optical pyrometers, one in the temperature range 700 to 1200°C by vanishing filament optical pyrometer (H & B Company) and another in the temperature range 300 to 500°C by infrared optical pyrometer (model R-38D, Raytek, USA). The accuracy of the temperature that can be expected by these pyrometers is ± 10°C. A calibration chart is prepared between the susceptor temperature and plate current of the oscillator valve.

All the glass-ware units including bubbler, inlet and outlet units, resistance and induction heating chemical reactors are enclosed in a closed aluminium chamber with perspex windows as shown in Figure 2-2. An exhaust fan is connected to the aluminium chamber. Two external exhausts are used separately one for bubbler and another for reaction chamber without any external pumping.

2.2.6 Some remarks on the fabrication of CVD system

In the present work, we have performed all the experimentation mainly with the resistance furnace since the induction heater was assembled only in the final stages of the work.
Even though we have incorporated various units for different film reactions, the system is mainly utilized with pyrolysis and oxidation reaction processes.

Various metal oxide thin films like tin oxide from stannous chloride and oxygen, chromium oxide from chromium (III) acetylacetonate, titanium oxide from tetraisopropyl orthotitanate have been prepared by using this system apart from aluminium oxide films obtained from aluminium isopropoxide.

Aluminium oxide thin films prepared by using this system have been studied by other workers for microstripline overlay\textsuperscript{391} to reduce the total power loss and secondary electron emission yields with very thin films. Tin oxide films are studied for electroluminiscence properties.

However, the present work is restricted to the study of optical properties of aluminium oxide films only.

2.3 Preparation of aluminium oxide thin films using MOCVD technique

Our main interest is to prepare aluminium oxide films for the study of optical properties, especially their dependence on the MOCVD process parameters.

The aluminium oxide films using this process were prepared earlier by many workers (see section 1.4.2) but used for the study of electrical properties for microelectronics applications. The thin films by MOCVD(Metal-organic chemical vapour deposition)process can be
deposited at low substrate temperatures (< 500°C) which offers more advantageous to study for optical applications.

The aluminium oxide films are deposited on various glass and silicon substrates by using MOCVD technique with a resistively heated horizontal displacement flow reactor system. The aluminium isopropoxide is used as a source (reactant) material.

The details of the source materials and the experimental details of the deposition procedures for homogeneous aluminium oxide films are given in the following subsections. A novel 'MOCVD Process' is described briefly for the deposition of graded-index aluminium oxide films.

2.3.1 Pyrolysis process and general deposition parameters

Aluminium oxide films are deposited by pyrolysis process using metaloxy-organic compound, aluminium isopropoxide. The thermal decomposition reaction of aluminium isopropoxide is given by

\[ \text{[Al(i-OC}_3\text{H}_7\text{)}_3\text{]}_2 \rightarrow \text{Al}_2\text{O}_3 + 3\text{C}_3\text{H}_7\text{OH} + 3 \text{C}_3\text{H}_6. \]  

The reaction mechanism for the formation of aluminium oxide films with the above reaction is given in section 1.4.3.

The general deposition parameters involved in the deposition of aluminium oxide films by MOCVD are divided into two categories, namely (A) adjustable process parameters (with step wise increment) and (B) some fixed parameters related to the design of MOCVD set-up itself.

The various adjustable process parameters under category (A) are (i) the reactant (bubbler) temperature, \( T_r \) (alternatively from which
the vapour pressure of reactant, aluminium isopropoxide can be estimated), (ii) the substrate temperature \( T_s \), (iii) the flow rate \( F_c \) of the carrier gas (the gas which transports the reactant vapours from the bubbler to reaction chamber), (iv) the flow rate \( F_d \) of diluent gas (the gas which dilutes the reactant vapours and also adjusts the total required gas flow rate in the reaction chamber, (v) the flow rate \( F_r \) of reactant gas (for example, oxygen which activate the reaction at the substrate surface) and (vi) the total deposition time.

The other fixed parameters under category (B) are : (i) geometry of the reaction chamber and type of heating (ii) geometry and position of the substrates in the reaction chamber and the substrate material (iii) inclination of substrate holder towards the inlet side of the reaction chamber, and (iv) the system pressure.

The geometry of the reaction chamber is fixed as described in section 2.2.5.1 and the substrate heating is resistance heating. Usually four glass substrates (size 2.5 cm x 2.5 cm) are placed on top of the St. steel plate. In some cases ten glass substrates (size 1 cm x 2.5 cm) are used as shown in Fig. 2-5. The front edge of St. steel plate is positioned at a distance of 24 cms, from the inlet of the reaction chamber. All deposition runs reported here are performed at zero inclination. For higher inclination (between 1 to 3°), we have found the film-non-uniformity at the edges of the substrate. Finally, the system pressure is one atm. pressure.

Different thin film depositions have been made under different sets of process parameters in category (A) to study various optical
properties. A typical example for the preparation of homogeneous film is given in section 2.3.3 whereas, the other details are given in Chapter 3.

2.3.2 Materials and substrates

Aluminium isopropoxide, in the form of white crystalline lumps, is obtained from Samarth Chemicals, Bombay (India). The material available in the form of powder is found to be not suitable for film deposition. The chemical is used after double distillation. The purity of the compound is expected to be of the order of 99.9%. The melting point of the aluminium isopropoxide is 118°C and its vapour pressure is 5mm Hg at 134°C. This compound has attained a considerable commercial importance in industry. Also it is relatively cheap and easily available compound compared to other metal-organics of aluminium.

N₂ is used as a carrier and diluent gas as it does not react with aluminium isopropoxide. The purity of the IOLAR 2 nitrogen gas is more than 99.9% and further purification is performed as described in section 2.2.1.

The substrates used for the deposition of aluminium oxide films are (1) borosilicate (belgium) glass substrate (size :25mm x 25mm and 10mm x 25mm; thickness, 0.9mm, nₛ = 1.52 at 632.8nm; maximum operating temperature, 450°C for 10 minutes), (2) Corning 7059 glass substrate (size : 15mm x 28mm, thickness, 0.5 mm; nₛ = 1.53 at 632.8 nm; maximum operating temperature 550°C) (3) fused silica substrate (size 10mm x 25mm; thickness, 1.2 mm; nₛ = 1.458 at 587.5 nm; maximum operating
temperature, 1050°C) and (4) silicon substrate (single crystalline polished on one side size: 10mm x 10mm; thickness, 525 μm, $n_s = 3.882$, $k_s = 0.019$ at 632.8 nm). Silicon wafers (phosphorous doped, 3-6 $\Omega$ cm) are of either <100> or <111> orientation.

In general the glass substrates are cleaned as described in the following steps (i) initially the glass substrates are cleaned with detergent solution (ii) rinsed with distilled water (iii) dipped in chromic acid solution with few drops of sulphuric acid and kept for 10 min (iv) rinsed again with distilled water and (v) dried under heating lamp.

The silicon substrates are cleaned with hot nitric acid (at 50°C) and then rinsed with distilled water. The substrates are dipped for few seconds in hydrofluoric acid solution and finally rinsed with the distilled water.

The MOCVD set-up, shown in Fig 2-4, is cleaned before and after the deposition of aluminium oxide films. The bubbler, inlet and outlet units are cleaned sequentially with isopropyl alcohol, tap water, ultrasonic cleaning and finally with the distilled water.

2.3.3 Sequence of operation of MOCVD set-up for the preparation of homogeneous aluminium oxide films.

The optimization of the process parameters to obtain homogeneous films with uniform thickness requires a detailed experimentation which is described in chapter 3 (section 3.2). A typical set of optimized deposition process parameters for the preparation of homogenous films is given in Table 2-1.
<table>
<thead>
<tr>
<th>Series</th>
<th>Adjustable process parameters in category (A)</th>
<th>Materials, if any</th>
<th>Deposition conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Reactant (bubbler) temperature $T_r$</td>
<td>Reactant: aluminium isopropoxide</td>
<td>$T_r = 145^\circ C$</td>
</tr>
<tr>
<td>2.</td>
<td>Substrate temperature $T_s$</td>
<td>Substrates: borosilicate glass</td>
<td>$T_s = 400^\circ C$</td>
</tr>
<tr>
<td>3.</td>
<td>Flow rate $F_c$ of the carrier gas</td>
<td>Carrier gas: Nitrogen</td>
<td>$F_c = 1.5 \text{ l/min}$ (liter per minute)</td>
</tr>
<tr>
<td>4.</td>
<td>Flow rate $F_d$ of the diluent gas</td>
<td>Diluent gas: Nitrogen</td>
<td>$F_d = 9 \text{ l/min}$</td>
</tr>
<tr>
<td>5.</td>
<td>Flow rate $F_r$ of reactant gas</td>
<td>Reactant gas: Oxygen</td>
<td>-</td>
</tr>
<tr>
<td>6.</td>
<td>Deposition time</td>
<td>-</td>
<td>10 min</td>
</tr>
</tbody>
</table>
The sequence of operation of MOCVD set-up for a typical deposition run is described in the following steps:

**Step 1**: The reaction chamber and all the glassware are cleaned and kept dried. Then high temperature grease is gently applied to all glass connectors. The glass substrates are cleaned as described in section 2.3.2. The substrates are placed on a stainless steel plate which is kept on a borosilicate glass stand as shown in Fig. 2-5. This stand along with the substrates is loaded in to the middle of the reaction chamber. The entire set-up is assembled as shown in Fig. 2-4.

**Step 2**: A charge of 10 gms of aluminium isopropoxide, crushed from the crystalline lumps, is inserted into the bubbler. Since the material is hygroscopic, the nitrogen is immediately flushed through the bubbler via Exhaust II (see Fig 2-4) for 5 min at the flow rate of 2 l/min. The reaction chamber is also flushed by N₂ via Exhaust I for 5 min at the flow rate of 5 l/min. Then all the inlet and outlet stopcocks of bubbler and reaction chamber are closed.

**Step 3**: The required reactant temperature (150°C) for bubbler and substrate temperature (375°C) for resistance heating are set by respective temperature controllers. The temperature of the inlet and outlet tubes of bubbler are also kept at about 150°C by means of a heating cord.

**Step 4**: After attaining the required temperatures, the flow rate \( F_c \) of the carrier gas passing through the bubbler is set for 1.5 l/min and the vapours from the bubble are by-passed through the Exhaust-II. The flow rate \( F_d \) of the diluent gas is set for 9 l/min and the reaction chamber is flushed by nitrogen through Exhaust I. This
process is continued for nearly more than 10 minutes, such that both the reactant and substrate temperatures attain the set values within + 2°C.

**Step 5:** With all the steady set temperatures and flow rates, the bypass to the bubbler is shut-off and the reactant vapours are allowed to pass through the reaction chamber for a specific time (10 min.) so as to obtain the required film thickness.

**Step 6:** After the completion of the deposition time, the reactant vapours are shut-off and by-passed again to Exhaust II. The reaction chamber is flushed by nitrogen (diluent) for 5 min to maintain a inert atmosphere in the chamber. Finally all gases are shut-off, all stopcocks are closed and the samples are allowed to cool down slowly.

### 2.3.4 A novel MOCVD process for the preparation of graded-index aluminium oxide films

Preparation of graded-index aluminium oxide films are achieved by a novel 'MOCVD process' adopted by us. With this 'MOCVD process' gradients within the thickness of thin film are intentionally introduced by varying the process parameters continuously during the deposition time. This method is somewhat different to that of Jacobsson's method of mixing of coevaporated films continuously during the deposition time.

The present preparation of graded-index thin films involves a two-stage process. In the first stage under different set of MOCVD process parameters (with stepwise increment of each parameter systematically keeping the others constant) various refractive indices are obtained or homogeneous films. In the second stage certain process parameters are selected for continuous variation to produce
graded-index thin films.

More details of the 'MOCVD process' on the preparation of graded-index aluminium oxide film are described in Chapter 4. In this section we give only a typical example to illustrate the process. A typical set of deposition process parameters for the preparation of graded-index aluminium oxide films is given in Table 2-II.

The sequence of operation for the preparation of graded index aluminium oxide films is same as that of homogeneous films given in the above section 2.3.3, except step 5. In step 5 (for the preparation homogeneous film), the substrate and reactant temperatures and flow rates of diluent and carrier gases are kept constant (or steady) throughout the deposition period. However, for the preparation of graded-index aluminium oxide thin film, after achieving the required initial substrate temperature \( T_{Si} \), the substrates are then allowed to cool down continuously by natural cooling up to a final substrate temperature \( T_{Sf} \) during the film deposition period. The rest of the parameters (i.e. \( T_r \), \( F_c \) and \( F_d \)) are kept constant during the deposition time.
### TABLE 2 -II PROCESS PARAMETERS FOR THE DEPOSITION OF GRADED-INDEX ALUMINIUM OXIDE THIN FILMS FOR A TYPICAL DEPOSITION RUN

<table>
<thead>
<tr>
<th>Series</th>
<th>Adjustable process parameters in category (A)</th>
<th>Materials, if any</th>
<th>Deposition conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Reactant temperature $T_r$</td>
<td>Reactant: aluminium isopropoxide</td>
<td>$T_r = 145^\circ C$</td>
</tr>
<tr>
<td>2.</td>
<td>Continuous variation of substrate temperature from initial substrate temperature $T_{si}$ to final substrate temperature $T_{sf}$</td>
<td>Substrate: borosilicate glass</td>
<td>$T_{si} \rightarrow T_{sf}$ $450 \rightarrow 350^\circ C$</td>
</tr>
<tr>
<td>3.</td>
<td>Flow rate $F_c$ of the carrier gas</td>
<td>Carrier gas: Nitrogen</td>
<td>$F_c = 1.5 \text{ L/min}$</td>
</tr>
<tr>
<td>4.</td>
<td>Flow rate $F_d$ of the diluent gas</td>
<td>Diluent gas: Nitrogen</td>
<td>$F_d = 9 \text{ L/min}$</td>
</tr>
<tr>
<td>5.</td>
<td>Flow rate $F_r$ of the reactant gas</td>
<td>Reactant gas: Oxygen</td>
<td>-</td>
</tr>
<tr>
<td>6.</td>
<td>Deposition time</td>
<td>-</td>
<td>12 min.</td>
</tr>
</tbody>
</table>
2.4 Optical measurements of aluminium oxide films

In the present work, the optical properties of aluminium oxide films are studied by using Abeles', ellipsometric and spectrophotometric methods. The general considerations, from the point of view of graded-index thin films, with the later two methods are already described in section 1.8. The measurement and the analysis procedures are given briefly in the following sections. The measurement procedures are virtually same for both homogeneous and graded-index thin films. But they differ in the analysis procedure. These techniques are most suitable and convenient for the analysis of both homogeneous and graded-index films and are easily available.

The thickness measurement by Fizeau fringes method is also included in these optical measurements, for completeness.

All the computer programs used in the optical analysis are briefly outlined in Table 2-V. The system NEC 1000 has been used for the computation.

2.4.1 Fizeau fringes method: measurement of film thickness

The measurement of film thickness by this method requires a step in the film down to the bare substrate, which is obtained by the following chemical etching process.
2.4.1.1 Formation of step

For the measurement of thickness by Fizeau fringes method and the refractive index by Abeles' method, the formation of a step on the film deposited on the substrate is essential. To form a step, the film is partially dipped in orthophosphoric acid H₃PO₄ (88-93%), at 60°C for few minutes by fixing the other end of the substrate to an adjustable stand. Then the film is immediately rinsed with distilled water and dried. It is found that, in the measurement of film thickness by Fizeau fringes method, the partial etching of the film by liquid provides a good gradual step between the film and the substrate as required.

2.4.1.2 Measurement of film thickness

Fizeau fringes method of measuring the film thickness is simple and is a commonly used technique. This method (also known as Tolansky technique) was developed to a remarkable degree by Tolansky for thin film work. It uses the interference effects arising when two partially reflecting surfaces are brought to close proximity. When a wedge of small angle is formed between substrate on which partly coated film with the film step and Fizeau plate (partially reflecting plate), illuminated by monochromatic light, broad fringes are seen, arising from interference between the light beams reflected from the surfaces on the two sides of the, air wedge. At points along the wedge when the path differences between those beams is an integral number of wavelengths, bright fringes are seen. Where the path difference is an odd number of half-wavelengths, dark fringes occur. The film thickness is given by \( d = \frac{d''}{D'} \cdot \frac{\lambda}{2} \), where \( d'' \) is fringe displacement at film
step and $D'$ is fringe width.

In this work, the thickness of film is measured by observing Fizeau fringes, in a conventional microscope equipped with micrometer eyepiece (Wild, Heerbrugge, 15xSK) and Fizeau plate attachment. The Fizeau plate attachment is equipped with three adjustable screws to determine the tilt of the plate relative to the specimen and thus control the direction and spacing of the interference fringes. A collimated monochromatic light of wavelength, $\lambda = 546$ nm is used as a source.

Accurate thickness measurement depends upon careful evaluation of fringe fractions. The evaluation requires a linear measurement, the accuracy of which is highly dependent on the definition and sharpness of the fringes. This would require (1) the Fizeau plate to be optically flat with high reflectivity and low absorptivity (2) extremely flat, smooth film surface and (3) very well collimated and narrow band of monochromatic light.

With our experimental set up the estimated error in measuring the film thickness is $\pm$ 5%.

2.4.2 Abeles' method: measurement of refractive index

At Brewster's angle,

$$\varphi_B = \tan^{-1}(n) \quad (2.4-1)$$

where $n$ is the refractive index of the film, the parallel component of the light reflected at the air-film interface vanishes$^{390}$. With non-absorbing uniform thin films the Brewster angle method due to Abeles
is most commonly used. This method requires a step in the film down to the bare substrate. Using the parallel component of light, Brewster's angle is then given by, that angle at which the intensity of the light reflected from the two surfaces (bare substrate and one coated with the film) is equal. Heavens\textsuperscript{138} has been shown that the greatest accuracy of measurement is obtained when the layer is an odd number of quarter-waves thick at the appropriate angle of incidence. This is because there is then the greatest difference in the reflectances of the coated and uncoated substrate. On transparent substrates with refractive indices not much different from that of the film (\(n_S \leq n + 0.3\)), the point at which the two reflectivities are equal can be determined easily by visual observation to obtain a refractive index accuracy to the third decimal.

In the present work, the refractive index of the film is obtained by Abeles\textsuperscript{1} method using a spectrometer, whose master circle could be read to an accuracy of 20 sec of arc. The sodium lamp is used as a source (\(\lambda = 589.6\) nm). A polaroid sheet (Edmunds, New Jersey) is used as a polarizer. All the substrates used in this method are frosted with emery powder prior to deposition on the rear side of the coated surface. The step in the film is obtained by etching, described in section 2.4.1.1.

2.4.3 Ellipsometry: measurement of refractive index and film thickness

The principle and theory of the ellipsometer is described in section 1.6 and 1.8. Here, a brief description is made about ellipsometer we used. The measurement procedure for \(\Psi\) and \(\Delta\) is also
The analysis procedures for homogeneous and graded-index films are given in the following subsections.

2.4.3.1 Description of the ellipsometer

We have used Gaertner's ellipsometer (Model L119X) the schematic diagram of which is shown in Fig. 2-6. (This facility is available to us at National Chemical Laboratory, Poona). The polarizer and analyzer are of 14mm diameter Glan Thompson prisms. The compensator is a quarter-wave mica plate at $\lambda = 632.8$ nm. A 10 mw HeNe laser (Hughes, Model 3222 HPC) is used as a monochromatic source (632.8 nm), along with adjustable laser mount, depolarizer and spatial filter. Extinction setting can be carried out either with the help of naked eye using Gauss eyepiece or solid state detector (model L118 D) along with a microammeter (model L118PM). In the Gaertner's ellipsometer, the prisms are equipped with 16 cm diameter circles can be read to an accuracy of 0.01 degrees. The master circle of the spectrometer has a flexibility for selecting any incident angle to an accuracy of 20 sec of arc.

2.4.3.2 Measurement procedure

The alignment of the spectrometer, calibration of the polarizer, analyzer and quarter plate circle have been performed as suggested by Archer. The schematic representation of ellipsometer, shown in Fig.2-6 is a PCSA (Polarizer, Compensator, Sample and Analyzer) system with reference to source and detector.

To reduce the back reflection the rear side of the glass substrates are frosted for ellipsometric measurements. In some cases,
FIG. 2-6: Schematic representation of Gaertner ellipsometer
transparent substrates are also used, but a black adhesive tape is stuck to the rear side of the substrate.

All the ellipsometric angles \( P, A, \gamma \) and \( \Delta \) are expressed in decimals.

The procedure for the measurement of \( \gamma \) and \( \Delta \) is as follows:

(a) Both the arms are set for some incident angle (usually for glass substrates the angle of incidence is kept at 50\(^\circ\) since the Brewster angle for glass used is 56.66\(^\circ\))

(b) A warm-up time of 10 minutes is given after laser source is turned on

(c) Sample is placed on the adjustable table and it is adjusted so that the light source is at centre through analyzer and sample table

(d) Analyzer and polarizer are slowly rotated manually to get minimum intensity of light (compensator is set at 45 at the time of calibration). Analyzer and polarizer are slightly rotated for complete extinction either by eye or by observing least intensity reading on detector ammeter.

(e) The first analyzer and polarizer extinction readings are noted down as \( A_1 \) and \( P_1 \) respectively.

(f) To the first polarizer extinction reading, 90 is added and the polarizer is set to this sum-reading, i.e. \( (P_1 + 90) \).

(g) The first analyzer extinction reading, \( A_1 \) is subtracted from 180 and the analyzer is set to the difference of \( (180 - A_1) \).

(h) At this setting the light should again extinguish. If not, the analyzer and polarizer are slightly rotated to get complete extinction. The second analyzer and polarizer extinction readings are recorded as \( A_2 \) and \( P_2 \) respectively. (When the actual second polarizer and analyzer readings are within 4 degrees of the calculated values \( P_2 = 90 + P_1 \) and \( A_2 = 180 - A_1 \), then the measurement accuracy is more for \( \gamma \) and \( \Delta \)).

(i) The values of \( \gamma \) and \( \Delta \) are calculated as follows:
\[ \rho = \frac{180 - (A_2 - A_1)}{2} \]  
\[ \Delta = 360 - (P_1 + P_2) \]  

**2.4.3.3 Analysis procedure for homogeneous films**

The determination of refractive index and film thickness for homogeneous aluminium oxide film from ellipsometric \( \rho \) and \( \Delta \) is carried out by either one of the two ellipsometric methods\(^{285} \), (i) determination of \( n \) and \( d \) by comparing the experimental \( \rho \) and \( \Delta \) to the theoretically obtained tabulated data of \( \rho \) and \( \Delta \) for various film thicknesses and refractive indices (computer program CP1, see Table 2-V), or (ii) direct determination of \( n \) and \( d \) from the experimental \( \rho \) and \( \Delta \) using an ellipsometric method (computer program CP2, see Table 2-V).

In both the cases, the film thicknesses obtained by Fizeau fringes method are compared with those obtained by ellipsometry.

For the determination of \( n \) and \( d \) by using method (i), a range of refractive indices (for aluminium oxide films) between 1.54 to 1.70 (with an increment of 0.001) and a range of thicknesses between 1 nm to 400 nm (with an increment of 1 nm) are assumed in the preparation of ellipsometric tables. The calculations are made at a wavelength \( \lambda = 632.8 \) nm and an angle of incidence \( \phi = 50^\circ \) for glass (\( n_g = 1.52 \)) and silicon (\( n_g = 3.882, k_s = 0.019 \)) substrates.

Using the method (ii), out of two solutions of thicknesses and refractive indices, one value of refractive index and thickness are chosen to the nearby thickness obtained by Fizeau fringes method. The sample data are given in Table 2-III.
### TABLE 2-III ELLIPSOMETRIC ANALYSIS OF HOMOGENEOUS FILMS

(A) Indirect method:

<table>
<thead>
<tr>
<th>Film thickness d by Fizeau's method (nm)</th>
<th>Experimental values</th>
<th>Calculated values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \gamma )</td>
<td>( \Delta )</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>308.9</td>
<td>12.58</td>
<td>184.30</td>
</tr>
<tr>
<td>295.6</td>
<td>11.90</td>
<td>185.10</td>
</tr>
</tbody>
</table>

(B) Direct method:

<table>
<thead>
<tr>
<th>Film thickness d by Fizeau's method (nm)</th>
<th>Experimental values</th>
<th>Solutions obtained by direct method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \gamma )</td>
<td>( \Delta )</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>141.6</td>
<td>13.75</td>
<td>174.14</td>
</tr>
<tr>
<td>509.5</td>
<td>11.43</td>
<td>185.15</td>
</tr>
</tbody>
</table>

\( \lambda = 632.8 \text{ nm} \); \( \phi = 50^\circ \); \( n_s = 1.52 \)
2.4.3.4 Analysis procedure for graded-index films

The top and bottom refractive indices of the graded-index thin films $n_t$ and $n_b$, and film thickness $d$ can be determined ellipsometrically as mentioned in section 1.8.2.

We have initially followed an ellipsometric method used by McCrackin\(^{276}\) and recently by Nakata and Kajiyama\(^{280}\) to evaluate the optical constants of graded-index thin films. The film with graded refractive index profile, normal to the substrate surface can be treated theoretically by dividing the graded-index film into a number of thin homogeneous sublayers. To achieve a result essentially independent of the number of layers\(^{257}\), it is necessary to have $d'/\lambda$ less than $5 \times 10^{-3}$, where $d'$ is the sublayer thickness. The convergence of $\psi$ and $\Delta$ on the increasing number of sublayers is shown in Fig 2-7. It can be seen from the Fig. 2-7 that the $\Delta$ is more sensitive to number of sublayers than $\psi$. We have assumed the number of sublayers to be 200. Rouard's method\(^{213}\) is followed in which the reflection coefficients are calculated from the substrate onwards and step by step through the intervening layers to the top of the multilayer system, to determine the values of $\psi$ and $\Delta$. We have used the McCrackin's multilayer program\(^{285}\) on ellipsometry for the calculation of $\psi$ and $\Delta$ (computer program CP3, see Table 2-V). Various tables of $\psi$ and $\Delta$ are prepared for graded-index aluminium oxide films on glass assuming different film thicknesses and gradient index ranges. In all cases a linear index profile is assumed. Here also $\phi_o = 50^\circ$ and $\lambda = 632.8$ nm.
FIG. 2-7: Convergence of $\Delta$ and $\gamma$ on increasing number of sublayers ($1.56 \rightarrow 1.66$; $\theta_0 = 50^\circ$; $n_s = 1.52$; $d = \lambda = 600$ nm)
Fig 2-8 gives a typical plot of $\psi$ versus $\Delta$, for film thicknesses between 115 nm to 350 nm, of graded index thin film with negative degree of inhomogeneity, where $n$ increases from top to bottom with 1.56 $\rightarrow$ 1.66 variation. Fig 2-8 also gives $\psi$ versus $\Delta$ curves of two homogeneous films having the top and bottom refractive indices corresponding to the above graded-index film i.e. with $n$ equal to 1.56 and 1.66 respectively. The calculations for $\psi$ and $\Delta$ are made on glass substrate ($n_g = 1.52$) at $\lambda = 632.8$nm and angle of incidence $\phi_0$, 50$^\circ$.

The $\psi_s$ and $\Delta_s$ values of glass substrate are 180.0 and 10.19. It can be observed from the Fig 2-8 that the value of $\psi_{\text{min}}$ of graded-index thin film where $\Delta$ is 180.0, is less than that of $\psi_s$ and it can be used as a test for the identification of inhomogeneity in thin film.

The procedure for the determination of $n_t$ and $n_b$ and film thickness $d$ is given below.

(i) The $\psi$ and $\Delta$ of graded-index films are obtained from the ellipsometric measurements as described in section 2.4.3.2.

(ii) The film thicknesses of graded-index film are measured by Fizeau fringes method as described in section 2.4.1.

(iii) The apparent refractive index $\tilde{n}$ and the apparent film thickness $\tilde{d}$ are obtained from the experimental $\psi$ and $\Delta$ by using 'homogeneous film model' as described in section 2.4.3.3. Anomalous values of $\tilde{n}$ and $\tilde{d}$ indicate the presence of inhomogeneity in the thin film.

(iv) The $\psi$ and $\Delta$ values measured by ellipsometry are examined for the values of $\psi$ and $\Delta$ that match those tabulated by the method indicated above for graded-index films with linear index profile. The film thickness obtained by Fizeau fringes method is also compared.
FIG. 2-8: Δ vs. Φ CURVES FOR LINEAR GRADED-INDEX FILM (1.56 -> 1.66) WITH NEGATIVE INDEX VARIATION (- - -) AND HOMOGENEOUS FILMS WITH n EQUAL TO 1.56 and 1.66 (— ). THE THICKNESS INCREASES IN THE DIRECTION OF ARROWS (ABOUT 100 TO 350 nm )
Thus the extreme refractive indices, i.e. top and bottom layer refractive indices are obtained by this method along with the film thickness. The sample data are shown in Table 2-IV.

2.4.4 Spectrophotometry: spectral measurements

The transmittance and reflectance of aluminium oxide films coated on glass substrates are measured by using UV-V spectrophotometer. These measurements are performed to obtain the important optical constants like refractive index $n(\lambda)$, extinction coefficient $k(\lambda)$, optical homogeneity and inhomogeneity of aluminum oxide films in the visible region (360 nm to 860 nm). In the following subsections a brief description of the spectrophotometer is given along with its performance checks. The measurement and analysis procedures for homogeneous and graded-index thin film are also described.

2.4.4.1 Spectrophotometer and its performance checks

UV-V-NIR spectrophotometer (model 330, Mfd. by Hitachi, Japan) is used for spectral measurements. The light emitted from the light sources (deutariam or tungsten lamp) is passed through two grating monochromators for obtaining a monochromatic beam, and then it is split into two beams. After passing through the sample and reference compartments, the monochromatic beams are converged and then converted into an electric signal by a detector, photomultiplier or PbS cell. The detector signal is amplified by a preamplifiers and digitized by a 16-bit A/D converter. At all the subsequent stages, the signal is processed by a CPU and the computational result is displayed directly
Table 2-IV  ELLIPSOMETRIC ANALYSIS OF GRADED-INDEX FILMS

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Experimental values of thickness d (nm)</th>
<th>Homogeneous model</th>
<th>Inhomogeneous model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Film thickness index</td>
<td>Apparent film thickness</td>
</tr>
<tr>
<td>1</td>
<td>237.6</td>
<td>1.467</td>
<td>225</td>
</tr>
<tr>
<td>2</td>
<td>107.6</td>
<td>1.617</td>
<td>110</td>
</tr>
</tbody>
</table>

\[ \lambda = 632.8 \text{ nm} ; \phi_o = 50^\circ ; n_s = 1.52 \]
TABLE 2 - V OUTLINE OF COMPUTER PROGRAMS USED IN THE OPTICAL ANALYSIS OF THIN FILMS

<table>
<thead>
<tr>
<th>Program code</th>
<th>Technique</th>
<th>Input data</th>
<th>Output data with variables</th>
<th>Method and remarks if any</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP1</td>
<td>Ellipsometric</td>
<td>( n, d, \lambda, \phi_0 ) ( n_o, n_s ) ( C )</td>
<td>( \gamma(n, d, \lambda, \phi_0) ) ( \Delta(n, d, \lambda, \phi_0) )</td>
<td>Indirect method</td>
<td>(285)</td>
</tr>
<tr>
<td>CP2</td>
<td>Ellipsometric</td>
<td>( n_0, n_s, \lambda, \phi_0 ) ( n, d ) ( C )</td>
<td>[ [n], [d] ] [ [n], [d] ]</td>
<td>Direct method, film thickness is to be selected out of the two solutions</td>
<td>(285)</td>
</tr>
<tr>
<td>CP3</td>
<td>Ellipsometric</td>
<td>( n_t, n_b, d, \lambda, \phi_0 ) ( n_o, n_s ) ( C ), ( N )</td>
<td>( \gamma(d, \lambda, \phi_0) ) ( \Delta(d, \lambda, \phi_0) )</td>
<td>Rouard's multilayer method, Linear, Exponential and Hyperbolic index-profiles</td>
<td>(285)</td>
</tr>
<tr>
<td>CP4</td>
<td>Spectrophotometric</td>
<td>( R_{fs}, R'<em>{fs}, T</em>{fs} ) ( R_{fs}, T_{fs}; d, \lambda ) ( \phi_0 = 0 ) ( C )</td>
<td>( n(\lambda), k(\lambda) )</td>
<td>Initial range of n &amp; k (301,307) are required. Results obtain with multiple solutions</td>
<td>(301,307)</td>
</tr>
<tr>
<td>CP5</td>
<td>Spectrophotometric</td>
<td>( n_t, n_b, d, \lambda ) ( n_o, n_s ) ( \phi_0 = 0 ) ( C )</td>
<td>( R_f(d, \lambda) ) ( (-) )</td>
<td>WKBJ approximation, Linear index profile</td>
<td>(229)</td>
</tr>
<tr>
<td>CP6</td>
<td>Spectrophotometric</td>
<td>( n_t, n_b, d, \lambda ) ( n_o, n_s ) ( \phi_0 = 0 ) ( N )</td>
<td>( R_f(d, \lambda) ) ( (-) )</td>
<td>Multilayer matrix method</td>
<td>(131)</td>
</tr>
<tr>
<td>CP7</td>
<td>Spectrophotometric, Ellipsometric</td>
<td>( n_t, n_b, d, \lambda, \phi_0 ) ( n_o, n_s ) ( C ), ( N )</td>
<td>( R_f(d, \lambda, \phi_0) ) ( T_f(d, \lambda, \phi_0) ) ( \gamma(d, \lambda, \phi_0) ) ( \Delta(d, \lambda, \phi_0) ) ( (+), (-) ) ( R_f(d, \lambda) ) ( (-) )</td>
<td>Extended the program CP3 for ( R_f ) and ( T_f )</td>
<td>(285,268)</td>
</tr>
<tr>
<td>CP8</td>
<td>Spectrophotometric</td>
<td>( n_t, n_b, d, \lambda ) ( n_o, n_s ) ( \phi_0 = 0 ) ( (-) )</td>
<td>( R_f(d, \lambda) ) ( (-) )</td>
<td>Exact solutions. Hyperbolic index profile</td>
<td>(255)</td>
</tr>
<tr>
<td>CP9</td>
<td>Spectrophotometric</td>
<td>( n_t, n_b, d, \lambda ) ( n_o, n_s ) ( \phi_0 = 0 ) ( (-) )</td>
<td>( R_f(d, \lambda) ) ( (-) )</td>
<td>Exact solutions. Exponential index profile</td>
<td>(225)</td>
</tr>
</tbody>
</table>

(C) : Complex refractive indices can be used.
(N) : Number of sublayers are to be indicated.
(+), (-) : Program can be used only for negative gradient variation.
(+) : Program can be used for both positive and negative gradient variations.
In model 330, the wavelength range is 187 nm to 2500 nm. The wavelength accuracy is $\pm 0.2$ nm for UV-VIS region and $\pm 1$ nm for NIR region. Photometric accuracy is $\pm 0.3\%$ transmittance. Resolution is 0.07 nm (for UV-VIS region). The base line flatness is within $\pm 0.2\%$ transmittance for UV-VIS region. Wavelength accuracy is checked as described in the instruction manual. As for the performance check a peak is obtained at 656.0 nm as expected (The peak wavelength should normally be located within a range of 656.3 to 655.9 nm and it was calibrated with line spectrum of D$_2$ lamp, 656.1 nm). Resolution check is also performed by scanning the instrument using D$_2$ lamp to a wavelength range of 656.3 to 655.8 nm and a line spectrum is obtained as expected.

2.4.4.2 Measurement procedure and reflectance corrections

Various spectral quantities used in this work, are represented as shown in Fig 2-9 with and without the second surface of the substrate frosted. Three experimental quantities, i.e. (i) transmittance of the film coated on transparent substrate, $T_{fs}$ (ii) reflectance of the film coated on transparent substrate, $R_{fs}$ measured from film side and (iii) reflectance of the film coated on transparent substrate, $R'_{fs}$ measured from the substrate side, are obtained by using spectrophotometry. For some samples, the rear side of the coated substrate is frosted to diffuse the light. The reflectance of the film coated on transparent substrate, $R_f$ is measured from the film side.

The transmittance, $T_{fs}$ is recorded between wavelength range 360 nm to 860 nm with air as reference. The spectrum is recorded using
FIG. 2-9. REPRESENTATION OF SPECTRAL QUANTITIES FOR
(a) Bare substrate & (b) Film supported on substrate.
The normal incident reflectances, \( R_{fs} \), \( R'_{fs} \) and \( R_f \) are obtained by using spectrophotometer with "5° specular reflectance attachment" (Hitachi, part No.210-0762). Two identical vacuum coated aluminium films on silicon (polished) substrates are used as reference and sample for initial base line correction. Aluminium is used as reference in all reflectance measurement of aluminium oxide films. The reflectance spectrum is recorded with response time as 4 sec and slit width of 4 nm to obtain a smooth curve on the recorder. The scan speed is 60 nm/min and the chart speed is 20 nm/cm. The wavelength range used is 360 nm to 860 nm. The reflectance spectra as recorded are termed as \( \bar{R}_{fs} \), \( \bar{R}'_{fs} \) and \( \bar{R}_f \) instead of \( R_{fs} \), \( R'_{fs} \) and \( R'_f \) since the measured reflectance spectrum requires some corrections (due to instrumental errors in the case of reflectance measurements). The normal incidence reflectance \( \bar{R}_{fs} \) of the aluminium oxide film coated on transparent glass substrate, light incident from the substrate side, is obtained just by reversing the sample in the measurement of \( \bar{R}_{fs} \).

The recorded values of \( \bar{R}_{fs} \), \( \bar{R}'_{fs} \) and \( \bar{R}_f \) can be converted into values \( R_{fs} \), \( R'_{fs} \) and \( R_f \) by using the following equations:

\[
R_{fs} = \bar{R}_{fs} \left( \frac{R_{ss,c}}{R_{ss,f}} \right) \quad (2.4-4)
\]

\[
R'_{fs} = \bar{R}'_{fs} \left( \frac{R_{ss,c}}{R_{ss,f}} \right) \quad (2.4-5)
\]

\[
R_f = \bar{R}_f \left( \frac{R_{s,c}}{R_{s,f}} \right) \quad (2.4-6)
\]
where \( R_{sf}, \) and \( R_{sf}^* \) are the measured reflectances of the standard (fused silica) with and without frosted second surface and \( R_{ss,c} \) and \( R_{ss,c}^* \) are the calculated reflectances for the same. The dispersion curve for fused silica (standard) is given by\(^{386}\):

\[
\frac{n_s^2(\lambda)}{\lambda^2} - 1 = 0.69617 \frac{\lambda^2}{\lambda^2 - 0.0046792} + 0.46704 \frac{\lambda^2}{\lambda^2 - 0.013512} + 0.89748 \frac{\lambda^2}{\lambda^2 - 97.93}
\] (2.4-7)

for wavelengths measured in microns.

To eliminate the second surface reflections of the transparent substrate the following equations are used to get \( R_f, R_f^* \) and \( T_f \) from the \( R_{fs}, R_{fs}^* \) and \( T_{fs} \) at each wavelength. These are given by\(^{307}\):

\[
R_f = R_{fs} - \frac{R_{ss}^2 T_{fs}/[(1-R_s)^2 + R_s (R_{fs}^* - R_s)]]}{T_{fs}}
\] (2.4-8)

\[
R_f^* = (R_{fs}^* - R_s)/\tan^2(1-R_s)^2 + R_s (R_{fs}^* - R_s)
\] (2.4-9)

\[
T_f = (1-R_s)T_{fs}/\tan(1-R_s)^2 R_s^2 R_{fs}^* (R_{fs} - R_s)
\] (2.4-10)

where \( R_s \) is the surface reflectance of the substrate without second surface and \( \tan \) is the internal transmittance of the substrate. The substrate equations are given by

\[
R_s = \{ \frac{T_{ss}^2 + 1 + R_{ss} (2-R_{ss})}{-\sqrt{T_{ss}^2 + 1 + R_{ss} (2-R_{ss}))^2 - 4R_{ss} (2-R_{ss})}/2(2-R_{ss})}
\] (2.4-11)

\[
\tan = \frac{R_{ss}^2 - R_s}{R_s T_{ss}}
\] (2.4-12)

The other substrate equations used in the conversion are given by\(^{303}\).
\[ n_S = \frac{(1 + R_S)}{(1 - R_S)} \quad (2.4-13) \]

\[ R_S = \frac{(n_S-1)^2}{(n_S + 1)^2} \quad (2.4-14) \]

\[ R_{ss} = R_S \left[ 1 + \frac{1}{R_S} \right] \frac{T_i^2}{(1 - R_S^2 \ T_i^2)} \quad (2.4-15) \]

\[ T_{ss} = \frac{T_i (1 - R_S)^2}{(1 - R_S^2 \ T_i^2)} \quad (2.4-16) \]

Conversely, the quantities \( R_{fs}, R'_{fs} \) and \( T_{fs} \) can also be written in terms of \( R_f, R'_f \) and \( T_f \) as

\[ R_{fs} = R_f + \frac{T_f^2}{(1 - R_f^2) \ T_i^2} \quad (2.4-17) \]

\[ R'_{fs} = R_S + \frac{(1 - R_S)^2}{R_f^2} \quad (2.4-18) \]

\[ T_{fs} = T_f \frac{T_i (1 - R_S)^2}{(1 - R_f R_S \ T_i^2)} \quad (2.4-19) \]

The experimental values of spectral reflectance and transmittance of standard fused silica (Meller Griot) substrate are shown in Figure 2-10. The data of the calculated reflectance and transmittance of fused silica obtained by equation (2.4-7) are also shown in the same figure. It can be seen from the Fig 2-10 (a) that the experimental reflectance curve is slightly increased instead of decreasing towards the longer wavelength region. This may be partly due to the instrumental errors, specifically due to misalignment of mirrors in 'reflectance-attachment' or corrosion of mirrors due to ageing. (No attempt is made for fine alignment of the 'reflectance-attachment' and is used as supplied by manufacturer). The corrections are made for the reflectance curves as described above. The same corrections are applied to all subsequent reflectance measurements.
FIG. 2-10: The experimental and calculated spectral reflectances \( R_{ss,f} \), \( R_{ss,c} \) and transmittances \( T_{ss,f} \), \( T_{ss,c} \) of fused silica substrate.
The reflectances of transparent and frosted borosilicate glass substrates are shown in Fig 2-11(a) after applying the reflectance corrections. The transmittance of borosilicate substrate is shown in Fig 2-11(b). The dispersion curve for the borosilicate glass substrate is shown in Fig 2-12.

It is observed that the dispersion curve for annealed (at 400°C) borosilicate glass substrate is slightly increased throughout the wavelength region. The refractive index of the annealed sample is increased to an order of 0.002 to 0.444 throughout the wavelength range.

As an example, the spectral reflectances, $R_{fs}$ and $R'_{fs}$ and transmittance, $T_{fs}$ of homogeneous aluminium oxide film deposited on transparent borosilicate glass substrate are shown in Fig 2-13. The reflectance curves are drawn after applying the reflectance corrections using equation (2.4-4) and (2.4-5). The converted values of reflectance, $R_f$ and transmittance, $T_f$ of the homogeneous film, eliminating the second surface effects of the substrate are also shown in Fig 2-13. It can also be seen from the Fig.2-13 that the difference between $R_{fs}$ and $R'_{fs}$ is very small indicating that the absorption is negligible in aluminium oxide films.

Similarly, the spectral reflectances $R_{fs}$ and $R'_{fs}$ and transmittance, $T_{fs}$ of graded-index aluminium oxide film deposited on transparent borosilicate glass substrate are shown in Fig.2-14. The converted values of $R_f$ and $T_f$ of the graded-index aluminium oxide thin film eliminating the effects due to second surface of the substrate are also shown in Fig.2-14.
FIG. 2-11 The corrected spectral reflectances ($R_s$, $R_{ss}$) and transmittances ($T_s$, $T_{ss}$) of borosilicate glass substrate
FIG. 2-13 The spectral reflectance and transmittance of homogeneous aluminium oxide film with and without the second surface of the substrate.
FIG. 2-14 The spectral reflectance & transmittance of graded-index aluminium oxide film with and without second surface of the substrate.
2.4.4.3 Analysis procedure for homogeneous films

We have used two methods for determining the refractive indices of thin films from spectrophotometric measurements. In one case the film is assumed to be lossless and dispersionless and in the other case both are considered.

In the first case, when $k$ is zero and $n$ is constant with wavelength, the refractive index of the film is given by

$$n = \sqrt{n_s} \sqrt{(1 + \sqrt{R_{\text{max}}})/(1-\sqrt{R_{\text{max}}})} \quad n > n_s$$

or

$$n = \sqrt{n_s} \sqrt{(1 + \sqrt{R_{\text{min}}})/(1-\sqrt{R_{\text{min}}})} \quad n < n_s$$

(2.4-20)

where $n_s$ is the refractive index of the substrate and $R_{\text{max}}$ (or $R_{\text{min}}$) is the reflectance at quarter-wavelength or integral multiples in optical thickness.

If the thickness of a film, its reflectance $R_f$ and transmittance $T_f$, measured at normal incidence, are known, it is possible to derive the quantities $n$ and $k$ of the complex refractive index, $n-ik$. In practice the equations giving $R_f$ and $T_f$ explicitly in terms of the optical constants of the film and substrate are very complicated and have multiple solutions. It has been shown that the Tomlin's method for $(1+R_f)/T_f$ rather than Heaven's explicit formulae for $R_f$ and $T_f$ separately simplifies the computation. The Tomlin's method is used for determining $n(\lambda)$ and $k(\lambda)$ (though the extinction coefficient is a small quantity) for aluminium oxide film on glass substrate. The method assumes that the film is homogeneous. For a single film on substrate, $R_f$ and $T_f$ are related to film $(n,k)$
and substrate \((n_s, k_s)\) parameters by the formulae

\[
f_1(n, k) = (4n_0 n_s A_1)^{-1} \left\{ A_6 [A_2 \cosh(2 \phi_1) + 2A_4 \sinh(2 \phi_1)] + A_7 [A_3 \cos(2 \phi_1 + 2A_5 \sin(2 \phi_1))] - [(1 + R_f)/T_f] = 0 \right. \tag{2.4-21}
\]

\[
f_2(n, k) = (2n_s A_1)^{-1} \left\{ n[A_2 \sinh(2 \phi_1) + 2A_4 \cosh(2 \phi_1)] + k[A_3 \sin(2 \phi_1 - 2A_5 \cos(2 \phi_1))] - [(1 - R_f)/T_f] = 0 \right. \tag{2.4-22}
\]

where

\[
A_1 = n^2 + k^2; \quad A_2 = n^2 + n_s^2 + k^2 + k_s^2; \quad A_3 = n^2 - n_s^2 + k^2 - k_s^2; \\
A_4 = nn_s + kk_s; \quad A_5 = nk_s - n_s k; \quad A_6 = n_0^2 + n^2 + k^2; \\
A_7 = n_s^2 - n^2 - k^2; \quad \phi_1 = 2 \pi M kd/\lambda; \quad \phi'_1 = 2 \pi M nd/\lambda, \tag{2.4-23}
\]

d is the thickness of the film of complex refractive index \(n - ik\); \(\lambda\) is the wavelength at which \(R_f\) and \(T_f\) are measured; \(n_s - ik_s\) is the complex refractive index of the substrate, \(n_0\) is the refractive index of the medium from which the light falls on the film—this will usually be unity.

A computer solution of equation (2.4-21) and (2.4-22) can be obtained by using the experimental values of \(R_f, T_f, d, \lambda, n_s\) and \(k_s\). A range of reasonable values of \(n\) is assumed. It can be seen from the above equations that a single value of \(k\) can be found for a given \(n\). One may readily solve \(f_2(n, k) = 0\), finding \(k\) for a given value of \(n\), by successive approximation using Newton's method, since \(\partial f_2 / \partial k\) may be easily written down. Each value of \(n\) and the corresponding \(k\) is substituted in turn into \(f_1(n, k)\). When a change in sign of \(f_1(n, k)\) occurs a simple interpolation leads to the required solution of \(f_1(n, k) = 0\). Multiple solution may be obtained for different values of...
The procedure is repeated for the data pair of \( R'_f \) and \( T_f \) replacing the equations \( R_f \) by \( R'_f \) in equations (2.4-21) and (2.4-22). Finally, the \( n \) and \( k \) obtained from \( R'_f \) and \( T_f \), for a given wavelength, should lie in close proximity to values obtained from \( R_f \) and \( T_f \). A computer program (CP4) is made for these calculations (see Table 2-V).

Tomlin's method\textsuperscript{301} shows whether the film thickness has been under or over estimated and the behaviour of dispersion curve lead to the criterion for a correct solution, viz. that the film thickness can be adjusted to produce a complete single-valued dispersion curve over as wide range of wavelengths as possible. With this criterion, the film thickness may be accurately found, and any ambiguity in the determination of refractive index can be eliminated. In another method\textsuperscript{306}, extinction coefficients of slightly absorbing homogeneous thin films can be estimated from the experimental data of \( R_{fs} \), \( R'_{fs} \) and \( T_{fs} \) by using the following equation.

\[
\frac{(R_{fs} - R'_{fs})}{T_{fs}} = k\left(\frac{(n_0 - n_s)}{(2n_0 n_s)}\right)
\]

\[
(4\pi d/\lambda) \left( n^2 - n_0^2 \sin^2 \phi_0 \right) \left( n_0 n_s/n^2 - 1 \right)
- \left( 1 + n_0 n_s/n^2 \right) \sin(n^2 - n_0^2 \sin^2 \phi_0) \]

2.4.4.4 Analysis procedure for graded-index thin films

Spectrophotometric methods are useful in finding out the degree of inhomogeneity, top refractive index \( n_t \) and bottom refractive index \( n_b \) and also to estimate the index profile \( n(z) \) with film thickness \( d \).
of graded-index thin films as well as homogeneous thin films with small unknown inhomogeneities. The analysis and measurement techniques have been already described, in sections 1.6 and 1.8.1. In this section we describe various methods and analysis procedures that we have used in the determination of optical constants of graded-index thin films.

(i) The first test\(^{255}\) for non-absorbing graded-index thin films is to check whether the \(R_f\) (the reflectance of the film coated on transparent substrate, eliminating the effect of the second surface of the substrate) at half-wave phase thickness is less than that of \(R_s\) (reflectance of the bare glass substrate eliminating the effect of the second surface of the substrate).

The degree of inhomogeneity, \(\Delta n/<n>\) of graded-index thin film can be determined from the data of \(R_s\) and \(R_{\text{min}}\) (i.e. the minima \(R_f\)) and applying the eqn. (1.8-1). The difference between \(R_s\) and \(R_{\text{min}}\) indicates the extent of the degree of inhomogeneity.

If the mean refractive index \(<n>\) is known, then \(n_t\) and \(n_b\) can be obtained as\(^{245}\)

\[
\begin{align*}
n_t &= <n> + \Delta n/2 \\
n_b &= <n> - \Delta n/2
\end{align*}
\]  

(2.4-25)  
(2.4-26)

Since equation (1.8.1) is an approximate one, better estimation can be made for a linear refractive index-profile by comparing the experimental spectrum of \(R_f\) with the one calculated using equation (1.6-26) assuming various constants. In fact the equation (1.8-1) was derived from equation (1.6-26), which is a solution of WKBJ
approximation where the reflections in the interior of the film are neglected\(^{229}\) and the above case is applicable up to \(|\Delta n| \leq 0.1\). A computer program (CP5, Table 2-V) is made for the calculation of \(R_f\) using eqn. (1.6-26).

(ii) The reflectance and transmittance spectrum are obtained from multiple sublayer or multilayer matrix method\(^{131}\) by treating the graded-index film into a number of homogeneous sublayers as described in section 1.6.4. In this case the film is assumed as non-absorbing. A form slightly more convenient for computation can be obtained if the relations between the electric vectors in successive layers are expressed in terms of Fresnel coefficients, as is done by Abeles\(^{217}\).

The amplitude of the transmitted and reflected vectors in terms of the incident vectors for \(x\) layers in matrix form as

\[
\begin{pmatrix}
E^+_0 \\
E^-_0
\end{pmatrix} = \frac{(C_1)(C_2)\ldots(C_{x+1})}{t_1 t_2 \ldots t_{x+1}} \begin{pmatrix}
E^+_{x+1} \\
E^-_{x+1}
\end{pmatrix}
\]

where \((C_m) = \begin{pmatrix}
\exp(i \delta_{m-1}) & r_m \exp(i \delta_{m-1}) \\
\exp(-i \delta_{m-1}) & \exp(-i \delta_{m-1})
\end{pmatrix}\)

writing the matrix product

\[(C_1)(C_2)\ldots(C_{x+1}) = \begin{pmatrix}
a & b \\
c & d
\end{pmatrix}.
\]

The reflectance and transmittance are given by

\[
R_f = (E^-_0) (E^-_0)^*/(E^+_0)(E^+_0)^* = c \ c^*/(a \ a^*) \quad (2.4-30)
\]

\[
T_f = (n_{x+1}/n_0) \left[ (E^+_{x+1})(E^+_{x+1})^* / (E^+_0)(E^+_0)^* \right] \\
= (t_1 t_2 \ldots t_{x+1}) (t_1^* t_2^* \ldots t_{x+1}^*) / (a \ a^*) \quad (2.4-31)
\]
In the computation (CP6, Table 2-V) the number of sublayers are assumed as 300. A linear index profile is assumed.

(iii) Methods by which the derivation of the reflection coefficient for a single layer may be extended to the case of any number of layers have been given by Rouard 213, Crook 131 and Vasicek 219. Two approaches 131 were made by these authors. Since a single film bounded by two surfaces possesses an effective reflection coefficient and accompanying phase change, then such a film may be replaced by a single surface with these properties. Rouard starts with the film next to the supporting substrate and works step by step through the intervening layers to the top of the system. Vasicek starts with the top layer and moves downwards towards the substrate.

We have followed the Rouard's scheme 213 for calculating the reflectivity of the system as shown in Fig 2-15 starting with two films (for light travelling from $n_0$ to $n_2$) with Fresnel coefficients $r_1$, $r_2$, $r_3$ ($r_1$, $r_2$, $r_3$ are written instead of $r_{01}$, $r_{12}$, $r_{23}$ for the sake of simplicity) the amplitude and phase of the light reflected by the lower film ($d_2$) can be computed as given below. Writing $\beta_2$ for the real amplitude and $\beta_2$ for the phase, we have

$$
\beta_2 \exp (i\beta_2) = \frac{r_2 + r_3 \exp(-2i\beta_2)}{1 + r_2r_3 \exp(-2i\beta_2)}
$$

(2.4-32)

This is the effective Fresnel coefficient for the layer $n_2$ and is inserted into the corresponding expression for the Fresnel coefficient for the whole system which is now regarded as a film of thickness $d_1$ lying on a surface whose Fresnel coefficient is $\beta_2 \exp (i\beta_2)$. We thus have
FIG. 2.15: ROUARD'S SCHEME FOR DEALING WITH MULTIPLE SUBLAYERS
\[ \rho_1 \exp (i \beta_1) = \frac{r_1 + r_2 \exp (i \beta_2) \exp (-2i \delta_1)}{1 + r_1 r_2 \exp (i \beta_2) \exp (-2i \delta_1)} \] (2.4-33)

and on eliminating \( r_2, \beta_2 \) between (2.4-32) and (2.4-33) we obtain

\[ \rho_1 \exp (i \beta_1) = \frac{r_1 + r_2 \exp (-2i \delta_1) + r_3 \exp (-2i \delta_1 - 2i \delta_2) + r_1 r_2 r_3 \exp (-2i \delta_1)}{1 + r_1 r_2 \exp (-2i \delta_1) + r_1 r_3 \exp (-2i \delta_1 - 2i \delta_2) + r_2 r_3 \exp (-2i \delta_1)} \] (2.4-34)

considering now, a system of \( x \) layers the lowest layer \( n_x \) has an effective Fresnel coefficient given by

\[ \rho_x \exp (i \beta_x) = \frac{r_x + r_{x+1} \exp (-2i \delta_x)}{1 + r_x r_{x+1} \exp (-2i \delta_x)} \] (2.4-35)

On the forming the product of this expression with its complex conjugate, we obtain

\[ \rho_x^2 = \frac{r_x^2 + r_{x+1}^2 + 2r_x r_{x+1} \cos 2\delta_x}{1 + r_x^2 + r_{x+1}^2 + 2r_x r_{x+1} \cos 2\delta_x} \] (2.4-36)

\( \beta_x \) may also be easily found from the Fresnel coefficients at each interface and from the phase thickness of the film.

The \((x-1)\)th layer is then added giving an effective Fresnel coefficient

\[ \rho_{x-1} \exp (i \beta_{x-1}) = \frac{r_{x-1} + \rho_x \exp (i \beta_x) \exp (-2i \delta_{x-1})}{1 + r_{x-1} \rho_x \exp (i \beta_x) \exp (-2i \delta_{x-1})} \] (2.4-37)
\( P_{x-1} \) and \( \beta_{x-1} \) are calculated in the same way as for \( P_x \) and \( \beta_x \) and the process is repeated successively until the final coefficient \( P_1 \) is obtained for the whole system. The reflection coefficient of the system is then simply given by \( P_1^2 \) (since \( P_1 \) is the real amplitude).

In this case the layers are non-absorbing for which the Fresnel coefficients are real. A system of absorbing layers, for which the refractive indices are replaced by complex quantities and for which the Fresnel coefficients are complex can also be dealt in a similar way.

It should be mentioned that the McCrackin's multilayer program used for the calculation of ellipsometric reflection quantities and \( \Delta \) is based on Rouard's method.

The parallel (p) and perpendicular (s) components of reflectance \( (R_p, R_s) \) and transmittance \( (T_p, T_s) \) quantities (defined in eqn. 1.6-22) are calculated apart from the ellipsometric \( \gamma \) and \( \Delta \). The program for the calculation of transmission quantities is extended in a similar way to Rouard scheme for reflection quantities (see CP7, Table 2-V). The calculations are made for normal and oblique incidence and also for absorbing multilayers. Both non-absorbing and absorbing substrates are used for the calculation of reflectance and only non-absorbing substrates are used for transmittance. The calculations are made for graded-index films of negative as well positive degree of inhomogeneity. The advantage with the multilayer method is that the calculation can be made for any kind of index-profile by replacing the 'Do loop' for linear index-profile.

(iv) In limited cases the exact solutions of the wave equations are
available for the calculations of reflection and transmission coefficients of graded-index thin films. Jacobsson\textsuperscript{255} had given an exact solution for hyperbolic index-profile, at normal incidence for non-absorbing graded-index film. The hyperbolic profile is defined in terms of the variable \( z \) as,

\[
n(z) = \frac{n_t n_b}{n_b + \left(n_b - n_t\right) z/d} \tag{2.4-38}
\]

where \( d \) is the total film thickness. The matrix elements\textsuperscript{255} at normal incidence are

\[
m_{11} = \left(\frac{n_b}{n_t}\right)^{1/2} \left[ \cos\{mln(n_t/n_b)\} + \frac{1}{2m}\sin\{mln(n_t/n_b)\} \right]
\]

\[
m_{12} = -i \frac{z_0^2 \Pi d(n_t n_b)^{1/2}}{m (n_b - n_t)} \sin\{mln(n_t/n_b)\}
\]

\[
m_{21} = -i 2 \frac{\Pi d}{\lambda z_0} \frac{(n_t n_b)^{1/2}}{m(n_b - n_t)} \sin\{mln(n_t/n_b)\}
\]

\[
m_{11} = \left(\frac{n_t}{n_b}\right)^{1/2} \left[ \cos\{mln(n_t/n_b)\} - \frac{1}{2m}\sin\{mln(n_t/n_b)\} \right]
\]

where \( m \) is given by

\[
m^2 = \left[ 2 \frac{\Pi d}{\lambda (n_b - n_t)} \right]^2 - 1/4 \tag{2.4-39}
\]

The reflection and transmission coefficients can be obtained using equations (1.6-16) and (1.6-17) (see CP8, Table 2-V). \( \text{(v)} \) Monaco\textsuperscript{225} has given exact solutions in terms of Bessel functions for exponential index-profile. \( \text{[see CP9, Table 2-V]} \)

The index of the inhomogeneous medium \((z)\), of film thickness \( d \) is represented by
The intensity reflectance at normal incidence is given by

\[
R_i = \frac{(n_o n_s p + n_t n_b q)^2 + (n_o n_b u + n_t n_s v)^2}{(n_o n_s p - n_t n_b q)^2 + (n_o n_b u - n_t n_s v)^2}
\]  

(2.4-42)

where

\[
P = Y_o (\alpha) J_{o}(\beta) - J_o (\alpha) Y_o (\beta) \\
Q = J_1 (\alpha) Y_1 (\beta) - Y_1 (\alpha) J_1 (\beta) \\
U = Y_o (\alpha) J_1 (\beta) - J_o (\alpha) Y_1 (\beta) \\
V = Y_1 (\alpha) J_o (\beta) - J_1 (\alpha) Y_o (\beta)
\]

(2.4-43)

\[
\lambda = \frac{2 \pi n_t}{\ln(n_b/n_t)} \frac{d}{\lambda}; \quad \beta = \frac{2 \pi n_b}{\ln(n_b/n_t)} \frac{d}{\lambda}
\]  

(2.4-44)

2.5 Characterization of aluminium oxide films by using Electron Spectroscopy for Chemical Analysis (ESCA)

Electron Spectroscopy for Chemical Analysis (ESCA) has been used to find the physico-chemical properties and composition of homogeneous and graded-index aluminium oxide films deposited on silicon substrates. The measurement principles of ESCA is already described in section 1.9.1. This technique is selected since it is more suitable and convenient for the characterization of oxide films and also to find out the film inhomogeneity by depth-profile studies.

The chemical shifts and chemical state plot for aluminium and oxygen to aluminium ratios have been studied, in the case of homogeneous and graded-index aluminium oxide films, for both surface and depth-profile information. The measurement and analysis procedures are described in the following subsections.
2.5.1 Experimental

ESCA spectra are obtained with Model VG7, VG Scientific Ltd., UK, using the AlK$_{\lambda 1}$ line ($h\nu = 1486.6$ eV) as the exciting source. All experiments are performed at a pressure below $10^{-8}$ torr in both the analyser chamber and source region. The analyser is a retarding cylindrical mirror system. A pass energy of 50 eV is used. The samples are the homogeneous and graded-index aluminium oxide films deposited on single crystalline silicon substrates. The C$_{1s}$ photoelectron line (284.6 eV) is assigned as a reference for calibration.$^{329}$

The XPS general scans for aluminium oxide film deposited on silicon substrate before sputter ion etching, after 1st etch and at the interface of aluminium oxide film and silicon substrate are shown in Fig. 2-16. Even though the aluminium oxide films are deposited from metal organic compound, aluminium isopropoxide, the carbon present in the film is insignificant, as depicted in Fig. 2-17.

2.5.2 Chemical state plots

Wagner$^{359}$ had been introduced chemical state plots, in which the intense line position data from compounds of an element with Auger kinetic energies are plotted on the y-axis and photoelectron binding energies on the x-axis. According to Wagner$^{329}$ with core-type Auger lines, many compounds are well dispersed, and the array can be understood qualitatively in terms of electronegativity of bonding atoms and polarizability of the medium.
FIG. 2-16 XPS general scan for aluminium oxide film on silicon at different depths \( T_s = 400 \, ^\circ \text{C} \).
Figure 2-17 C\textsubscript{1}s line energy (uncorrected) at different depths for aluminium oxide film on silicon.
The basic chemical state plot as given by Wagner et al. for aluminium is shown in Fig. 2-18. Compounds with aluminium-oxygen bonds have data points in blank region of Fig. 2-18. The use of these data for chemical state identification requires that the unknown chemical states be present in uniform bulk environments of thicknesses at least several atomic layers. In chemical state plot, the grid of diagonal lines of slope +1 represents a grid of the Auger parameter $\alpha$ which in essence is the difference in energy between the Auger line and photoelectron line. This simple definition was modified by adding the photon energy, known as modified Auger parameter $\alpha'$ this makes the quantity independent of the photon energy used, and it is quickly calculated by adding the Auger kinetic energy and photoelectron binding energy.

The experimental data of aluminium oxide films have exhibited significant XPS Auger and photoelectron chemical shifts as shown in Fig. 2-16. The KLL Auger electrons of aluminium are generated by the bremsstrahlung component of the radiation, which can be usually obtained with conventional instrumentation (without monochromator). The chemical state plots of KLL Auger kinetic energy versus 2p photoelectron binding energy obtained for homogeneous and graded-index aluminium oxide films are given in sections 3.6 and 4.6 respectively.

2.5.3 Surface and depth profile quantitative analysis

Surface and depth profile quantitative analysis of homogeneous and graded-index aluminium oxide films are performed by using 'elemental sensitivity factors' method as first proposed by Wagner and Jorgensen and Berthou. In the case of 'elemental sensitivity
FIG. 2-18 Chemical state plot for aluminium
factors' method, intensities of peaks are referred relative to those of the standard for atoms in typical homogeneous environments. Division of peak height or peak area intensities by the appropriate sensitivity factors gives the relative number of atoms detected, on the assumption of sample homogeneity.

The XPS signal current can be written as

\[ I_{i,x} = N_i S_{i,x} \]  \hspace{1cm} (2.5-1)

where \( I_{i,x} \) is the measured current of photoelectrons of kinetic energy \( E_k (i) \) (the energy level \( x \) i.e. 1s, 2s, 2p of the \( i \) th i.e. O, Al elemental species) from the sample, \( N_i \) (i.e. \( N_O, N_{Al} \)) is the volume density of atoms of the \( i \) th species and \( S_{i,x} \) represents the XPS elemental sensitivity factor for the level \( x \) of the \( i \) th species from the sample. By using equation (2.5-1) the \( N_i \) can be calculated once the values of \( I_{i,x} \) and \( S_{i,x} \) are known. The quantity \( I_{i,x} \) is proportional to the XPS peak area or peak height. The surface composition, i.e. the ratio of \( N_O/N_{Al} \) can be calculated by using the reported data of elemental sensitivity factors and experimental data of peak areas or peak heights. This method is applied for the determination of surface composition in homogeneous and graded-index aluminium oxide films and the data are given in sections 3.6 and 4.6 respectively.