CHAPTER I

THIN FILM

Thin film technology plays a pivotal role in the development of such diverse and challenging frontiers as microelectronics, optical coatings and integrated optics, thin-film superconductivity and quantum engineering and surface science, engineering and technology, micromagnetism, metallurgical coatings, and amorphous materials.

Thin films can be regarded as matter, uniformly distributed between two parallel plates extended infinitely in two directions, the dimensions, however of the material being constant and restricted along the third direction i.e. the thickness. A film is basically a layer of any material, the word thin being usually added for films whose thickness is less than about 1 μm (10,000 $\overset{o}{A}$). A recent viewpoint is that a film can be considered thin or thick depending on whether it exhibits surface-like or bulk-like properties.

Optics enjoys the historical priority of being the first branch of physics to have been confronted with a thin film anomaly, in the form of coloured reflections from soap bubbles, oil patches on water etc. The work on optical films started at about 17th century, Joannes Marcus Marci (1648), Robert Boyle (1663), Robert Hooke (1665), but the real birth of thin film applications in optics took place only after the advent of advanced vacuum technology.

Modern day technology requires several types of thin films for a variety of applications.[1,2,3] The films can be single or multicomponent, alloy/compound or multilayer coatings on substrates of different shapes and sizes.[3-5] . The properties required of the films can be, depending on the applications, high optical reflection/transmission, hardness, wear resistance, single crystal nature etc. Such a versatility in thin films is brought about by the techniques of thin film deposition.

The basic steps involved in a thin film deposition technique are:

step 1. Creation of species.

step 2. Transport from source to substrate.

step 3. Film growth on the substrate.

Thin film deposition techniques have been broadly classified in four main categories:

(1) Physical vapour Deposition (PVD).

(2) Chemical vapour Deposition (CVD).

(3) Electrodeposition, Electroless or solution Growth Deposition.

(4) Polymeric coatings.

Since in this work thermal evaporation is used throughout, only PVD technique is elaborated in this chapter.

1.1   PVD TECHNIQUES.

The physical vapour deposition process encompasses the following techniques.

I)   Thermal evaporation/electron beam evaporation.

II)   Sputtering.

III)   Ion plating.

IV)   Ion assisted deposition.

V)   Molecular beam epitaxy (MBE).

VI)   Activated Reactive Evaporation (ARE).

All these deposition process require high vacuum environment for good quality thin films. One of the major advantages of PVD techniques is that, steps 1,2 and 3 of deposition can be independently controlled and therefore one can have a much greater degree of flexibility in controlling the structure and properties of film.

1.1.1   **THERMAL EVAPORATION**

Thermal evaporation is one of the most well known PVD techniques. It is a simple technique and one can evaporate a large variety of materials,(metals, semiconductors or dielectrics) on different substrates.

In thermal evaporation the material located in a source is heated by means of direct resistance, radiation, eddy currents, electron beam, laser beam, arc discharge etc. On heating a material in vacuum, it evaporates at a rate given by the well-known Langmuir-Dushman equation. The vapour atoms thus created are transported through vacuum to get deposited on the substrates. The ambient is vacuum because otherwise the vapour species will get scattered by collision with gas atoms. Only at pressures $\leqslant 10^{-5}$ Torr does the mean free path between collisions become large enough so

that the vapour beam arrives at the substrate unscattered. A low vacuum has an additional effect that the gas molecules strike the substrate and this can result in contamination of the films being deposited. The evaporation of materials is done in a vacuum system which in most cases comprises a diffusion pump backed by a rotary pump.

The evaporant material is supported on a source which is then heated to a sufficiently high temperature to produce desired vapour pressure ($\geqslant 10^{-2}$ Torr). In case of most of the materials, this temperature is in the range of 1000^0 to $2000^0 c$. The requirements for source materials are that, it should have a negligible vapour pressure at the deposition temperature and should not react with the evaporant. The shape of source should be such that it should be possible to hold evaporant materials in any available form.(powder, wires etc).

The film deposition is not uniform because the amount of material reaching the substrate depends on the angle (θ) between the source and the substrate area.[6] The rate of deposition follows a $\cos\theta/r^2$ variation for a point source (knudsen effusion cell) and $\cos^2\theta/r^2$ variation for evaporation from a small area,(r) being the distance between the source and the substrate. If a uniform thickness is desired, the substrate has to be rotated in a manner that each point on the substrate receives almost same amount of material during the deposition various thickness uniformity

models have been proposed by various workers.[7-10] The
thickness uniformity is influenced by the characteristics of
the vapour source (geometry, type etc).

One can evaporate from two or more sources in
order to deposit a multilayer film or an alloy/compound
film. In this case, in addition to a thickness variation,
there can be a composition variation. If a stoichiometric
compound/alloy film is to be deposited, the evaporation
rates from the two sources have to be carefully controlled.

1.2   **MECHANICAL PROPERTIES OF THIN FILMS.**

The mechanical properties of thin films are
strongly dependent on structure, microstructure, chemical
composition and incorporated impurities. They are
influenced by the production technology used and parameters
chosen. From the point of view of optical coatings, the
importance of mechanical properties of thin films is
primarily in relation to its stability that is the extent to
which coatings will continue to behave as they did when
removed from coating chamber, even when subjected to
disturbances.

The various mechanical properties are,

1)   Adhesion

2)   Stress

3)   Tensile Strength

4)   Hardness

1.2.1 ADHESION.

Adhesion is defined as the work necessary to separate the coating substrate interface.[11] The interfacial region between a coating and a surface largely determines the extent of durability of the films. Good adhesion is promoted by,

1) Strong atom-atom bonding within the interfacial region.

2) Low local stress levels.

3) Absence of easy deform. ation or fracture modes.

4) No long term degradation modes.

Adhesion can be categorized[12] as follows depending on the microstructure of the interface layer.

a) Mechanical interface layer : mechanically interlocking interface is formed due to porous nature of substrate.

b) Monolayer on monolayer : abrupt transition from film material to substrate material.

c) Chemical bonding : chemical reaction of film atoms with the substrate atoms.

d) Diffusion interface layer : partial solubility required between film and substrate material.

e) Pseudo diffusion interface layer; one type of interface layer seldom occurs alone. A combination of various types of interface layer often occurs simultaneously.

Adhesion of thin films is influenced by a large number of parameters :

I) Choice of coating and substrate materials.

II) Substrate preparation.

III) Coating method.

IV) Composition of residual gas at the substrate surface.

V) Stability of film substrate system.[13]

Adhesive forces can be classified as follows :

Physisorption.

Chemisiorption.

Chemical Bonding.

It has also been reported[14,15] that adhesion increases over a period of time. This was attributed to the slow formation of an electrostatic double layer and charging effect.[16]

1.2.1.1   METHODS TO DETERMINE ADHESION.

As given in table 1.2.1.1 it is seen that the mechanical methods of measuring adhesion are more obvious and direct. Fig 1.2.1.1 gives some of the methods of adhesion measurement. Some of the more commonly used adhesion measurement methods are described in brief.

1.2.1.1.1   SCOTCH TAPE METHOD.

This method was originally suggested by strong[18] in 1945. It consists of pressing a piece of adhesive tape to the film. When the tape is pulled off rapidly the film is either wholly removed, partially removed, or left behind on the substrate. The method is obviously only qualitative and gives no indication of the relative magnitudes of the adhe-

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Table 1.2.1.1
Methods of Adhesion Measurement

Qualitative	Quantitative
Mechanical Method	
Scotch tape test[18]	Direct pull off method[17]
Abrasion test[26]	Moment or topple test[19,23]
Bend and Stretch test[27]	Ultracentrifuge test[17,20]
Shearing Stress test[28]	Ultrasonic test[17]
	Peeling test[17,3,21]
	Tangential shear test[22]
	Scratch test[3,24,25]
Non-mechanical Method	
X-ray diffraction[4]	Thermal method[11]
	Capacity test[17]
	Nucleation test[3]

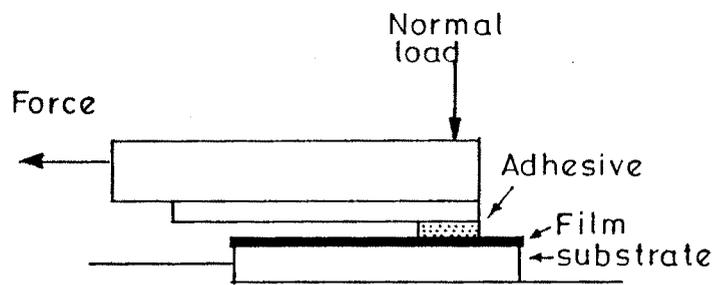The field of application of nonmechanical methods is very limited and complicated for technological applications.

Pulley

Film plus backing

To Synchronous motor

(a) The peel test

Auxillary weight

pivot

Diamond tip
Film
Substr-
ate
X-Y stage

(b) Schematic of the scratch test.

Stud

film

adhesive   substrate

(c) The direct pull off method

Force

adhesive

film
substrate

(d) The topple method

Normal load

Force
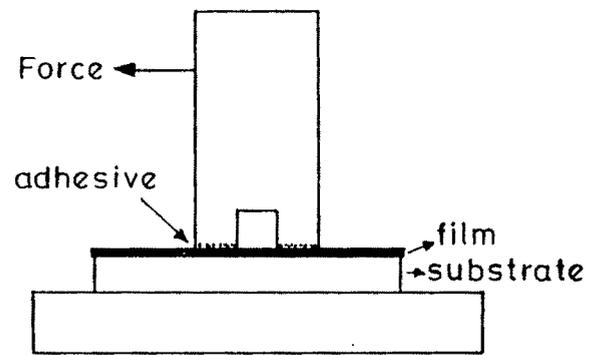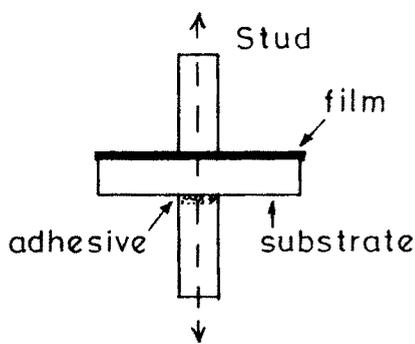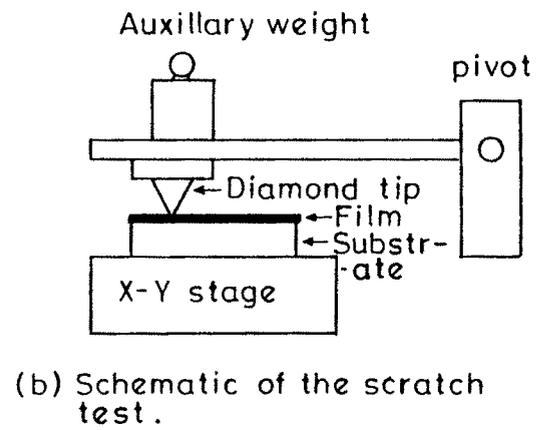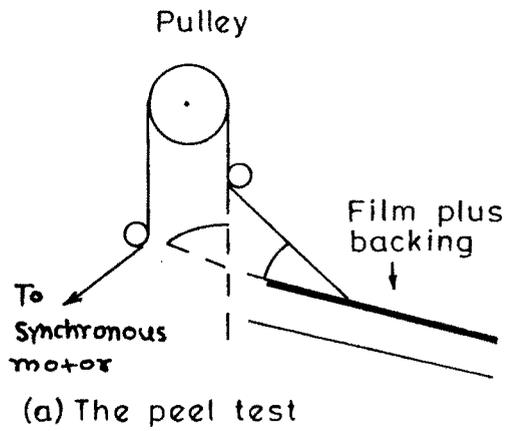
Adhesive

Film
substrate

(e) The tangential shear test

Fig. 1·2·1·1 — Methods of adhesion measurement.

sive forces,if the adhesion of the film to the substrate exceeds the adhesion of the tape to the film. If the film is removable, however, it is possible to turn the measurement into a quantitative one.

1.2.1.1.2 SCRATCH METHOD.

The first detailed work using a scratch method measuring adhesion was undertaken by Heavens[29] who used a smoothly rounded chrome-steel point which was drawn across the film surface. A vertical load was applied to the point and gradually increased until a critical value of the load was reached at which the film was completely removed resulting in a channel when examined under an optical microscope. The critical load at which clear track s are formed was taken as a measure of the adhesion.

1.2.1.1.3 ABRASION METHOD.

In this method the resistance is determined by rubbing the surface with an emery-loaded rubber[6,30] However, the mar resistance is found not only to be due to the hardness of the layer but also to depend on the adhesion. The technique has been turned into an adhesion-measuring system[31], by abrading evaporated metal films with a stream of fine silicon carbide particles dropped from a known height. The removal of the film was monitored by measuring the electrical resistance of the film. Differences in evaporation conditions and also annealing caused, changes of adhesion that could be detected.

1.2.1.1.4   **DIRECT PULL OFF(DPO) METHOD**.

Some kind of pulling device is attached to the film by means of an adhesive and film pulled in a direction perpendicular until fracture occurs at the film surface interface.[32]   The force per unit area of the film needed to cause adhesive failure at the   film-substrate interface is taken to be the measure of adhesion.

1.2.1.1.5   **MOMENT OR TOPPLE METHOD.**

This is a   variation of the direct pull off method. Here the force is applied in horizontal direction to a rod glued to the film, and the moment of the force required to break the   film from the substrate is a measure of adhesion.[19]

1.2.1.1.6   **ULTRACENTRIFUGAL AND ULTRASONIC METHOD.**

In ultracentrifugal method no adhesive or solder is used.The films are uniformly deposited onto cylindrical surfaces of small stainless-steel rotors.The rotors, which are approximately 0.1 in. diameter, are then magnetically suspended in a vacuum and spun   at higher and higher speeds until the film is thrown out.[32]

Ultrasonic vibration as a method of measuring adhesion has been examined by Moses and Witt.[33] At 50 KHz, accelerations of the order of 10^5 gr wt could be obtained, and this can be raised to 10^9 gr wt by using 10 MHz.

1.2.2   **STRESS**

Interest in the mechanical stresses in thin

films started as early as 1877,during the intervening years many stress determinations have been made in thin films produced by various methods.

Nearly all films, by whatever means they are produced, are found to be in a state of internal stress. The consideration of internal stress in thin films is of importance in the use of thin films for various purposes. These stresses can cause film rupture, loss of adhesion, substrate cracking, and change in the physical and chemical properties of the film. They also limit the film thickness. The stress may be compressive (i.e. the film would like to expand parallel to the surface) so that in extreme cases it may buckle up on the substrate. Alternatively the film may be in tensile stress (i.e. the film would like to contract), and in certain cases the forces may be high enough to exceed the elastic limit of the film so that it breaks up.

One of the most common process of stress is due to the unequal thermal expansion coefficients. Heating or cooling will produce additional stress which will tend to deform the film combination. This stress contribution is known as "Thermal stress"[3,34].

If the difference between the temperature of film during deposition and after deposition is ΔT then the thermal stress θ_T is,

$$\theta_T = (\Delta \alpha - \Delta T - \gamma_F)/(1 - \gamma_F)$$

where, $\Delta \alpha$ ------ Difference in the thermal expansion coefficient of film and substrate.

γ_F ------ Poisson ratio of film material.

Besides thermal stress, many films are found to have a residual internal stress due to the process of film growth and this part is called the "Intrinsic stress".[3,34] Thus the total stress S observed in a film is equal to the sum of any externally applied stress plus thermal plus intrinsic components.

i.e. $S = S_{external} + S_{thermal} + S_{intrinsic}$

In technological applications the total stress must be kept small. The intrinsic stress is the predominant component in many systems and has been the subject of most of the investigations.[23,25,34,35-38]

The annihilation of excess vacancies, dislocations, grain boundaries, phase transformations, compositional changes etc. are some of the processes which can produce additional stresses in the film and hence contribute to intrinsic stress.[39]

Various models have been suggested to explain the origin of intrinsic stress in the film.

1) The grain boundary growth.[40,41]

2) Grain boundary relaxation.[38,42]

3) Excess vacancy annihilation.[39]

4) Shrinkage of grain bounding voids.[39]

5)   Impurity effects. [36,38]

6)   Lattice misfit accommodation model. [43]

1.2.2.1   <u>STRESS MEASURING TECHNIQUES.</u>

If a deposited film is in stress on a thin substrate, the substrate will be bent by a measurable degree. A tensile stress will bend it so that the film surface is concave, and a compressive stress so that is convex.
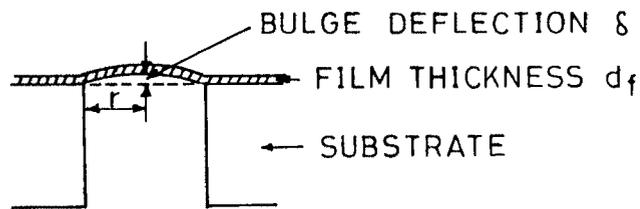
The most common methods for measuring the stress in a thin film are based on this principle. The deformation of the substrate due to the stress is measured either by using a thin cantilevered beam as a substrate and calculating the radius of curvature of the beam and hence the stress, from the deflection of the free end, or by observing the displacement of the center of a circular disk.

Stress may also be measured by X-ray or elec-tron-diffraction techniques. The common methods of stress measurement are given in fig.1.2.2.1.
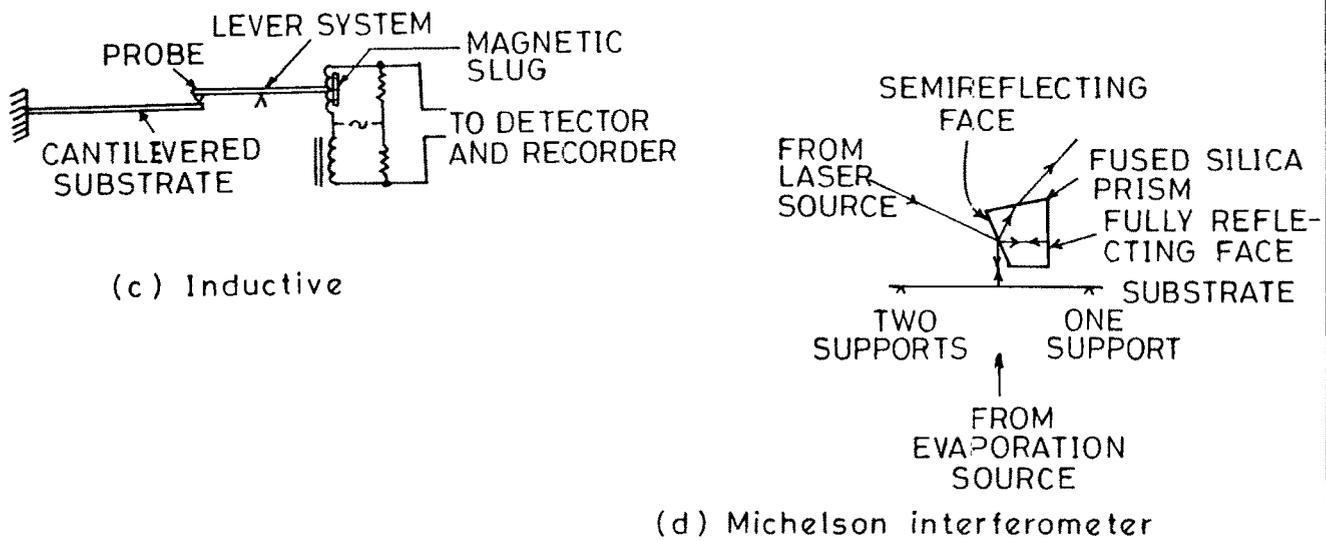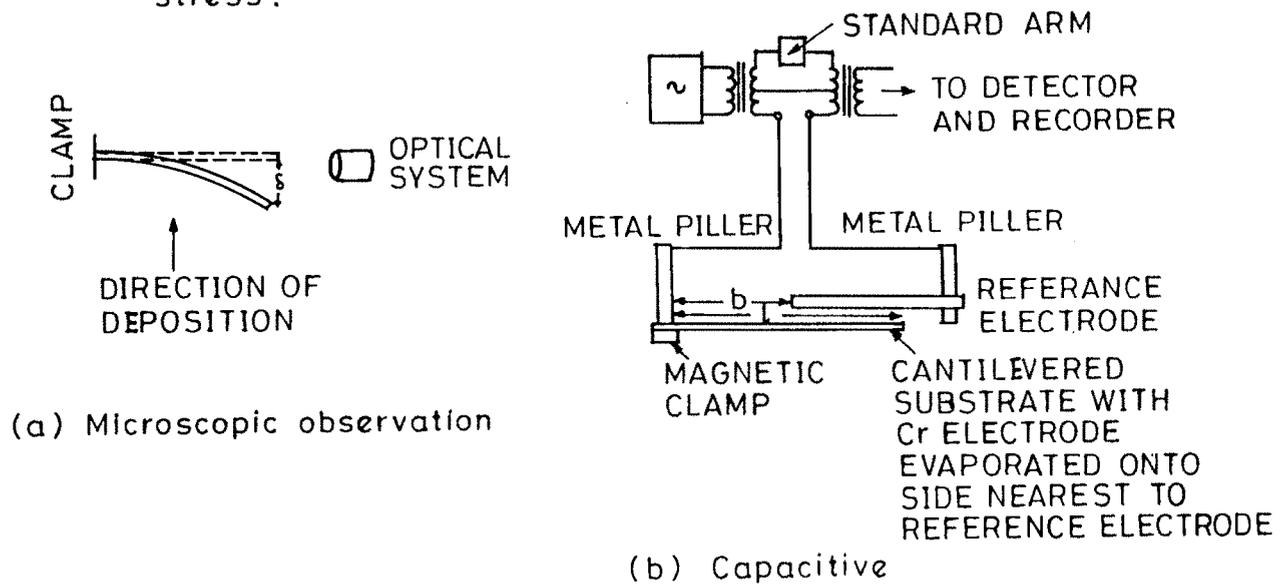
1.2.2.2   <u>DISK METHOD.</u>

In the disk method, the stress of a film is measured by observing the deflection of the center of a circular plate when the film is deposited on one side.

Disks strained by the presence of a film will bend into a paraboloid. The stress S can then be related to the deflection by the disk at a distance 'r' from the

BULGE DEFLECTION δ

FILM THICKNESS d_f

SUBSTRATE

1) Diagram of bowing of unsupported film in compressive stress.

(a) Microscopic observation

(b) Capacitive

(c) Inductive

(d) Michelson interferometer

Methods of measuring stress by bending technique.

Fig. 1·2·2·1 — STRESS MEASURING TECHNIQUE.

center of the disk,

$$S = (6/r^2) (E_s/3(1-\gamma)) (ds^2/df)$$

Where E_s = Young's modulus of substrate.

γ = poissons ratio for the substrate.

d_s = substrate thickness.

d_f = film thickness.

The method is not suitable for in-situ measurements.

Various observation techniques can be employed for observing the stress.

I) Pressure measurement[44] : metal disks are used and the bowing of the disk is observed hydrostatically by having a fluid in contact with one side of the disk and observing the movement in a capillary as a disk bowing.

II) Interferometric method : The interference fringes (Newton rings) between the disk and an optical flat are used to measure the deflection as the disk bows.

III) Optical[3] : measuring the reflected image of a slit using a light section microscope.

1.2.2.3. BENDING BEAM METHODS.

In the beam method, the substrate is usually between three to five times longer than it is broad. The beam curvature is found by measuring the deflection either of one end of the beam while the other end is clamped or of the middle of the beam if it is supported at both ends. The sensitivities of the various beam methods depend on the

detection systems used to observe this movement.

Various observation system can be used:

1. Microscopic observation of the movement of the free end.[3]

2. Contractometer - expansion or contraction of the spi-
    ral, detected by pointer.[45]

3. Electro mechanical restoration of beam to its original
    position.[3]

4. Capacitance change detected by bridge circuit.[37]

5. Hot wire current measured.[3]

6. Michelson interferometer detects movement of center of
    substrates.[46]

1.2.3.   TENSILE STRENGTH.[4]

The tensile strength is the maximum value of the breaking force per unit cross sectional area. Similar to stress measurement various methods are available for tensile property measurement. In most of these techniques the stress-strain data is obtained.

1.2.4.   HARDNESS.[47]

Hardness is defined as the amount of plastic deformation produced mainly in compression by a known force, the deformation varying from point to point in the region under the indenter.

1.3   OPTICAL PROPERTIES OF THIN FILMS.

1.3.1   INTRODUCTION.

The phenomenal growth of thin film research and

development owes much to the stimulus provided by the early utilitarian interest in the application of optical films in mirrors and interferometers.

The considerable theoretical and experimental investigations on the optical behavior of thin films deal primarily with optical reflection, transmission, and absorption properties and their relation to the optical constants of films. The reflection, transmission and interferometric properties of thin films have made it possible to determine the optical constants.

1.3.2 **THIN FILM OPTICS.**

The results for the amplitude and state of polarization of a light beam reflected and transmitted by a thin film in terms of the fresnel coefficients of reflection and transmission at the interfaces between the media and as a function of the optical constants, the film thickness, and the angle of incidence of the light beam.

It must be pointed out that these results are based on the assumptions that a thin film is a homogeneous, isotropic, and plane-parallel layer thickness t, which is comparable with the wavelength of light λ. The film is characterized optically by a refractive index (n) and extinction coefficient (k). It assumes the role of attenuation. Complex refractive index, $N = n-ik$.

1.3.3.   THEORY OF REFLECTION AND TRANSMISSION.

The procedure for calculating the fraction of the incident electromagnetic radiation reflected or transmitted from a film, consists of two basic steps.

1)   The form of electromagnetic field is found which satisfies the Maxwell's equation, and the material equations which specify the macroscopic properties of the material and the surrounding media.

2)   The solution of this equation is made to satisfy the appropriate boundary conditions.

The details of the calculations of the solutions are extensively available in standardtext books.[48-50].

1.3.4   OPTICAL COATINGS DEVELOPMENT AND TYPES.

The rapid progress in optical coatings could be achieved only after the advent of vacuum pumps in the early 1930's. Tremendous strides have been made in the field of optical coatings and they are increasingly gaining importance even in volume applications like displays, optical data storage, architectural coatings, lighting etc.

1.3.4.1.   VARIOUS TYPES OF OPTICAL COATINGS.

By a suitable choice of materials and deposition sequences, various types of optical coatings can be obtained. The basic principle used is interference phenomenon in the film and is naturally wavelength, thickness and angle of incidence dependent.

1.3.4.1 (a) ANTIREFLECTION COATINGS

These types of coatings are reflection reducing.[51] The need for antireflection coatings on the surfaces in optical system (e.g. telescope and camera lenses) is necessary for two reasons.

1)   Most of the reflected light at each surface is lost for the transmitted beam, and if there are either many reflecting elements or elements with high refractive index,such losses may be intolerable.

2)   The multiple reflections between the surfaces of the elements cause unwanted light to fall onto the image plane, thereby reducing the contrast and definition of the image.

Antireflection coatings can range from a simple single layer having virtually zero reflectance at one wavelength to a multilayer of twenty or more layers having virtually zero reflectance over a range of wavelengths.

1.3.4.1 (b) HIGH REFLECTING SYSTEMS.

The reflectance of a surface may be enhanced by the deposition of a single film of material of high refractive index of optical thickness quarter wavelength.[52] Under this condition the beams reflected from air/film and film/substrate interfaces are in phase.

Another application of selective reflection is the cold mirror [53 p-224] where a semiconductor is used as a substrate on which a quarter-wave stack is coated. This type of system has a high reflectance in the visible spec-

trum and high transmittance in the near infra red.

1.3.4.1 (c) INTERFERENCE FILTERS.

Filters are devices which have preferential transmission or reflection for different wavelengths. The term interference filters came into existence because all of them are governed by interference phenomenon. The basic interference filter is a fabry-perot type shown in figure 1.3.4.1 (c) 1.

By proper choice of the spacer layer thickness and material and also the reflecting layers, various types of filters like edge filters, narrow band, broad band etc.[60] can be constructed. Reflection filters can be broad band or narrow band filters, long wave pass and short wave pass.[54] Another type of filter construction possible is the frustrated total-reflection filter[55]. Fig 1.3.4.1 (c) 2 gives a frustrated total reflection filter. This type of filter reduces the losses arising from light scattering in the layers.

1.3.4.1 (d) THIN FILM POLARIZERS.

The need for an efficient polarizer of large aperture may be met in a quite suitable fashion by the use of thin transparent layers. By suitable choice of thickness and refractive index of a film and angle of incidence of light on the film, it is possible to arrange suppression of one of the polarized components and enhancement of the other.
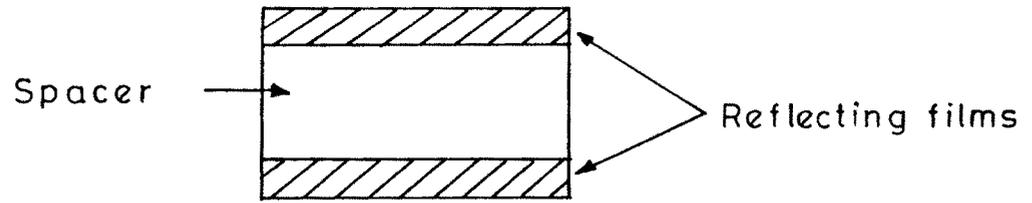
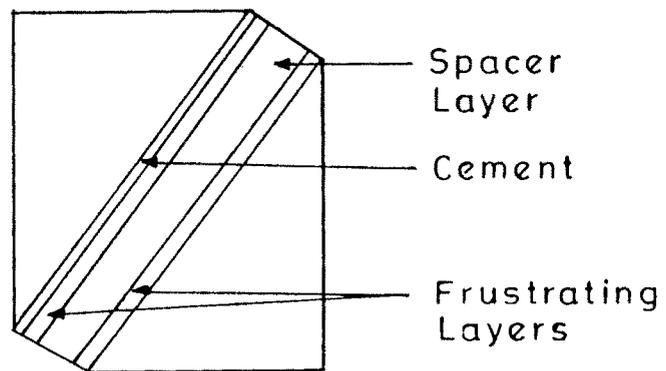Fig. 1·3·4·1 (c) 1 - The Interference filter.

Fig. 1·3·4·1 (c) 2 - Frustrated total reflection filter

1.3.4.1 (e) <u>OTHER OPTICAL COATINGS.</u>

Most of the coatings in this category are a combination of antireflection, high reflection properties. Some of the coatings in this class are,

a) Neutral beam splitters.

b) Neutral density filters.

c) Multiphase retarders.

d) Optical tunnel filter etc.

1.3.5   <u>MATERIALS USED IN OPTICAL COATINGS WITH SPECIAL</u>
<u>REFERENCE TO DIELECTRIC OXIDE FILMS.</u>

Useful materials for optical coatings assuming that they can be produced in the thin film form by vacuum deposition or related techniques must possess all or atleast some of the requirements mentioned below depending on the applications it is put to. The important factors are:

1) Refractive index and region of transparency.

2) Homogeneity and packing density.

3) Mechanical properties such as hardness, adhesion and the magnitude of any built-in stress.

4) Chemical properties such as solubility and resistance to attack by atmosphere and their compatibility with other materials.

5) Toxicity.

6) Price and availability.

There can be some other specific properties important in specific applications.

The films useful for optical coating can be

Table: 1.3.5(1)
Characteristics of Some Oxide Materials Used in Optical Coatings.

Sr.No.	Material	Evaporation Techique	Refractive Index	Region of Transparency (μm)	Remarks
01	Aluminium oxide Al_2O_3	Electron Bombardment (2050°C)	1.55-1.62	0.2-7	Hard & resistant can also be produced by anodic oxidation.
02	Antimony trioxide Sb_2O_3	Mo boat Electron Beam	2.04-2.29	300nm-1 m	Decomposes if over heated.
03	Bismut oxide Bi_2O_3	Reactive Sputtering of bismuth in O_2	2.45	-	Not studied much
04	Cerium oxide CeO_2	Tungsten boat, Electron beam (1600°C)	2.2	400nm-16 m	Tends to form inhomogeneous layer
05	Hafhium oxide (HFO_2)	Electron beam, Reactive deposition (2200°C)	2.0-2.15	220nm-12 m	Fairly hard
06	Lanthanum oxide (La_2O_3)	Boat, Electron beam, Reactive deposition (1500°C)	1.9-1.98	350 nm-72 m	To be deposited on hot substrate
07	Magnesium oxide (MgO)	Electron beam (2800°C)	1.7-1.74	0.2-8	Hard and resistant

cond......

Sr.No.	Material	Evaporation Techique	Refractive Index	Region of Transparency (μm)	Remarks
08	Neodymium oxide (Nd_2O_3)	Boat, Reactive evaporation (1900°C)	1.79-2.15	0.4-72	Decomposes at high boat temperatures
09	Silicon monoxide (SiO)	Boat (1300°C)	1.7-2.0	0.5-8	Fast evaporation at low pressure
10	Silicon dioxide (SiO_2)	Electron beam (~1600°C)	1.45-1.46	0.2-9	Hard when deposited on heated substrate
11	Tantalum pentoxide (Ta_2O_5)	Electron beam Reactive evaporation (2100°C)	2.1-2.25	0.35-10	Hard and resistant
12	Titanium dioxide (TiO_2)	Electron beam, Reactive evaporation (1750°C)	2.2-2.7	0.35-12	Can be produced by oxidation of Ti Films
13	Yttrium oxide (Y_2O_3)	Electron beam Boat	1.82	0.25-2	Hard
14	Zinc oxide (ZnO)	Boat	2.1	0.4-10	Soft
15	Zirconium oxide (ZrO_2)	Electron beam, Reactive evaporation	1.97-2.1	0.34-12	Hard

divided into two categories:

1)   Dielectric films.

2)   Metallic films.

The   work in this thesis deals with oxide   films so the literature survey concerns only these films.

Table 1.3.5 (1) gives some important data for some useful oxide materials in optical coatings.[54,57,58]

1.3.6   LIMITATIONS OF OPTICAL FILMS.

The   nonavailability of dielectric   films   with satisfactory optical 'and mechanical properties is a   serious limitation in the utility of these films for specific applications. Though multilayer coatings solve this problem to a certain extent, the manufacture of multilayers is in itself a very complicated and lengthy task needing very precise control of the various parameters.

In case of dielectric films a marked wavelength dependence[55] the films property is observed. The   adhesion of dielectric film is good, but due to their porosity they absorb water and age with time.[4]

The preparation of dielectric oxide films   which are hard and have good adhesion is not so easy as   fluoride and sulphide[6] films. Most oxides react with the crucible materials or dissociate at the required high temperature.[56]

1.3.7   AGING OF OPTICAL FILMS.

The   aging phenomenon in the case of optical

coatings is the changes in the optical characteristics with time during storage and use. The aging is manifested as a change in refractive index, absorption coefficient, appearance of cracks on the film, foggy appearances, drifts in passband etc. Various causes are attributed to aging. The major among them are:

1) Moisture.

2) Temperature.

3) Stress in the layer.

4) Recrystallisaion etc.

Other agents such as vibrations, shock, corrosive fluids etc. can also cause deterioration of the optical coatings.

Out of these, the factor that has considerable effect on the optical characteristic is moisture. The relative importance of moisture in relation to other factors is still an open question.

1.3.7.1   AGING SCALE.

According to the time required for the aging process to occur, aging can be classified as,

1) Seconds - and minutes - scale.

2) Hours - and days - scale.

3) Years - scale.

The seconds - and minutes - scale aging can be considered to be taking place inside the vacuum chamber

59,60

during the film deposition   and during air inlet into

the vacuum chamber after deposition.[61-64] These fast
changes of the first type are attributed to the
incorporation of moisture and other impurity atoms during
air inlet. The changes in the optical properties due to
moisture sorption leads to dynamic effects.[59]

Most of the literature found on the optical
properties of thin dielectric films are results of studies
undertaken after the films have been removed from the
deposition chamber. Apart from the dynamic changes taking
place during deposition, the most significant changes in the
properties take place during the first few days after
manufacture. These changes can continue for months
together.[65-68] These types of changes constitutes the hours
- and days - scale aging. The years scale aging though not
under-taken very often, finds use in determining the long
term utility of the optical coatings and components.

1.3.7.2   PACKING DENSITY.

One of the parameters usually used for
explaining the aging effect is the packing density. It is
well known that vacuum evaporated dielectric films have a
columnar porous microstructure.[69-71] The columns are
aligned in the direction of growth, in a more or less
closely packed structure. This means that the films are
composed of relatively well developed crystalline
aggregates, grain boundaries and vacant places such as
intermediate gaps and pores.

In order to study the effect of these pores on the film structure and properties, the knowledge of packing density is essential. The packing density Pm may be defined as,[72]

$$P_m = \frac{\text{Volume filled up with film material.}}{\text{Total volume}}$$

The packing density can be related to the refractive index through the Lorentz - Lorentz formula for refractive index of mixture.

If n_f denotes the refractive index of film, n_m - refractive index of bulk material then packing density can be written as,

$$Pm = \frac{(n_f^2 - 1)(n_m^2 - 1)}{(n_f^2 + 2)(n_m^2 - 1)} \qquad 1.3.7.2(1)$$

Various authors[69,72-76] have proposed various models for calculating packing density.

The concept of packing density helps in knowing about the stability of optical coatings. The higher the packing density the lesser the films will age.[69]

Various factors are responsible for the changes in optical properties of dielectric films. Some of the most influential parameters are dealt with in brief in the following sections.

1.3.7.3   EFFECT OF MOISTURE.

Films of most dielectric materials possess columnar structure.[69-71] If deposited near room

temperature, the columns are packed so that long pores reach from upper to the lower surface. The effect of atmospheric moisture on a single film is to rapidly fill the pores[71,77-81] with water, so that the refractive index and hence optical thickness changes.

The sorption of water can have a very strong effect on parameters like refractive index, stress, adhesion, hardness etc. Both reversible and irreversible changes takes place. Many moisture dependent anisotropic effects, in optical coatings have been studied by J. R. Gee etal[81] The analytical technique[75] for investigating water sorption in pores has been verified by various authors.[69,71,82] Water sorption is also known to cause additional tensile stress in the film.[83] The shift in the passband wavelength usually toward, the red end of spectrum has also been used to study the effect of moisture on the films.[80]

1.3.7.4   TEMPERATURE EFFECT.

Annealing carried out intentionally or occurring through use at elevated temperatures may lead to a change in packing density and refractive index.

According to Furman etal[84] the effect of temperature is to cause a displacement of the spectral curve. The nature and the direction of this displacement depend on the method of the filter preparation, condition of its

formation on the substrate and the subsequent thermal treatment.

The influence of temperature upon the optical properties of the films cannot be treated separately without regard for other factors like amount of moisture in pores, crystallization, tension,degree of interaction with the surrounding medium.[84] These factors may change the properties under the influence of temperature.

Many authors[85-88] have studied the influence of substrate temperature and annealing of dielectric films.

1.3.7.5 **STRESSES IN THE LAYERS.**

Thin films are generally in a state of mechanical stress (internal and external) during and after the deposition. Stresses arise from incomplete structural ordering process, from the chemical or physical incorporation of material and from differences in expansion coefficients of the film and substrate. The packing density has an important influence on the stress behavior of a thin film. Observation of crazing patterns that is network of cracks on dielectric films[89] have shown that the development of these patterns is accompanied by recrystallisation within the film structure.[23] The crazing process is accelerated by thermal stresses[90,91] produced by temperature cycling and by moisture.[38] A sequence of localised recrystallisation and elimination of voids leads to a stressed film.

1.3.7.6 <u>OTHER</u> <u>FACTORS</u>

In addition to the above mentioned factors their might be variations in the chemical composition through decomposition, dissociation and fractionation during evaporation process and through insufficient recombination a major problem encountered during oxide film deposition which may be the cause of non-stable optical properties.

Non-stoichiometric films[92] have vacancies which coalesce to form microcavities, and pores. These pores help in moisture adsorption in the films. The mechanism of absorption of high energy radiation[90] can also contribute to deterioration of optical coatings.

1.4 <u>REVIEW</u> <u>OF</u> <u>STUDIES</u> <u>ON</u> <u>CERIUM</u> <u>OXIDE</u> <u>FILMS.</u>

Cerium oxide (CeO_2) is a high refractive index material. P.Lostis[93] succeeded in depositing CeO_2 by thermal evaporation and also used it as a $\lambda/3$ layer on the hypotenuse of 45^0 prism to produce a $\lambda/4$ plate.[94] An increase in reflectance for Al mirrors in visible range on being coated with $\lambda/4$ film of $MgF_2 + CeO_2$ was observed by Hass.[95] Mixed films of $MgF_2 + CeO_2$ on Si has been used for infrared antireflecting coating.[96] Many authors[97-99] have evaporated dielectric mixtures of CeO_2 with MgF_2 or CeF_3 for various applications. Not much work has been done on the properties of cerium oxide films obtained by thermal evapo-

ration. Kersten[100] etal have studied the properties of evaporated CeO_2. The effect of heating of CeO_2 films in air is reported by smith etal[101] cerium oxide deposited by sputtering technique and authors[57,102-106] have reported value of refractive index ranging from 1.9-2.5 depending on various factors. Evaporation by electron-gun is also another techniques used for depositing CeO_2 films[56,107,108]

Netherfield etal[109] investigated the properties of electron beam evaporated CeO_2 films with simultaneous O_2 ion bombardment. Studies on ion assisted deposited CeO_2 films have been done by Robee etal[86,110].

1.5 TECHNIQUES FOR MEASURING VARIOUS OPTICAL CONSTANTS OF DIELECTRIC FILMS.

There are numerous methods available for measuring the optical constants. Some of the commonly employed techniques are only mentioned here.

The most widely used method are the Abele's method, spectrophotometer and ellipsometer.

1.5.1 ABELE'S TECHNIQUE.

This requires that a single substrate be partially coated with half the surface carefully masked. It compares the intensity of the reflected "P" polarized light from the coated and uncoated section.

1.5.2 SPECTROPHOTOMETRY.

The measurement of intensities of reflected and

transmitted radiation beam as a function of wavelength. There is no direct way of finding the refractive index of the films, for films which do not show a sharp peak.

1.5.3 ELLIPSOMETRY.

In this the effect on the polarisation of a monochromatic plane wave produced by the reflection on the sample surface is measured. This needs computer programming for data processing. The present work mainly deals with measurement taken on ellipsometer. The theory and working principle are elaborated in art. 1.6

1.5.4 WAVE GUIDE METHOD.

The principle of guided waves is used here. The requirement of substrate index lower than film index and coupling prism index greater than film index limits the applicability of this technique.

1.5.5 ENVELOPE METHOD.

This provides a method for investigating film inhomogeneity. This method is sensitive to film thickness nonuniformity and substrate non uniformity.

1.5.6 POLARIMETRY.

This technique involves the determination of the phase change on reflection (ϕ_R) or transmission (ϕ_T) by interferometric methods.

In the present work on optical properties of CeO_2 films, ellipsometer is used to measure the (Δ) and (Ψ)

values. The basic theory and working principle of ellipsometer is explained in brief in section 1.6

1.6   THEORY OF ELLIPSOMETER.

Ellipsometry is an optical method of surface investigation. A beam of polarized light is reflected from a surface and the change in the state of polarization is measured. This change yields two parameters usually called (Δ) and (Ψ), which describe the relative phase and amplitude changes of the components of the light wave parallel with and perpendicular to the plane of incidence. These two parameters give information on the optical properties of the reflecting system and the thickness of layers which might be present on the substrate.

The state of polarization of an incident monochromatic polarized beam (amplitude E) upon reflection (amplitude R) from a boundary between two media, is characterized by the ratio of electric field amplitudes parallel and perpendicular to the plane of incidence and by the phase difference between these two components. [111]

Denoting the parallel component by p and perpendicular component by s, the ratio of p and s amplitudes for incident (i) and reflected (r) waves are written for convenience as,

$$\tan \Psi_i = (|E_a^p|)/(|E_a^s|)$$

and   1.6.1

$$\tan \Psi_r = (|R_a^P|)/(|R_a^S|)$$

Where E's and R's are the amplitudes of incident and reflected light respectively.

On reflection, the amplitude ratio is changed by a factor,

$$\tan \psi = \tan \psi_\gamma / \tan \psi_i$$

$$= (|R_\alpha^p| / |R_\alpha^s|) / (|E_\alpha^p| / |E_\alpha^s|) \qquad 1.6.2$$

The reflection coefficients (r) in general complex numbers, are defined by,

$$r^p = \frac{|R_\alpha^p| \; e^{i \, \delta_\gamma^p}}{|E_\alpha^p| \; e^{i \, \delta_i^p}}$$

$$r^p = \frac{|R^p|}{|E^p|} e^{i (\delta_\gamma^p - d_i^p)} \qquad 1.6.3$$

$$r^s = \frac{|R_a^s| \; e^{i(\delta_{sr}^s)}}{|E_a^s| \; e^{i(d_{si}^s)}}$$

$$\frac{|R_\alpha^s|}{|E_\alpha^s|} e^{i(\delta_\gamma^s - \delta_i^s)} \qquad 1.6.4$$

Where δ's are the phases of the various components with reference to an arbitrary time origin.

A quantity reflectivity (ϱ) is defined as the ratio of the reflection coefficients of both the components.

$$\varrho = r^p / r^s$$

$$= \{[(|R_\alpha^p|) / (|E_\alpha^p|) /[(|R_\alpha^s|)/(|E_\alpha^s|)]]e^{i(\beta^p - \beta^s)}$$

where, $\beta^p = d_r^p - d_i^p$

and $B = d_r^s - d_i^s$

substituting the value of,

$$(|R_a^p|) / (|R_a^s|)$$

and $(|E_a^p|) / (|E_a^s|)$

we get,

$$\varrho = \frac{\tan\psi_r}{\tan\psi_i} e^{i(\beta^p - \beta^s)} \qquad 1.6.5$$

If (Δ) is the relative phase difference between p and s components after reflection,

i.e. $(\Delta) = \beta^p - \beta^s$ 1.6.6

ϱ can be written as,

$$\varrho = \tan\psi\, e^{i\Delta} \qquad 1.6.7$$

This is the basic equation of ellipsometry. The ellipsometry basically involves the measurement of (Δ) and (ψ).

Comparing this equation with equation for R^p and R^s from fresnels equation we have,

$$R^p = \frac{r_{af}^p + r_{fs}^p \exp D}{1 + r_{af}^p\, r_{fs}^p \exp D}$$

$$R^s = \frac{r^s_{af} + r^s_{fs} \exp D}{1 + r^s_{af} r^s_{fs} \exp D}$$

where,

$$D = (-4\pi i\, n_f\, d_f\, \cos\phi_f)/\lambda$$

$$\rho = R^p / R^s = \tan\psi e^{i\Delta} \qquad\qquad 1.6.8$$

$$\tan\psi e^{i\Delta} = \frac{(r^p_{af} + r^p_{fs} \exp D)(1 + r^s_{af} r^s_{fs} \exp D)}{(1 + r^p_{af} r^p_{fs} \exp D)(r^s_{af} + r^s_{fs} \exp D)}$$

Rearranging the terms gives a quadratic equation in D (which is effectively relative optical path in film).

$$C_1 (\exp D)^2 + C_2 \exp D + C_3 = 0 \qquad\qquad 1.6.9$$

Where C_1, C_2, C_3 are involved complex polarisation dependent functions of (Δ), (ψ) and r's , which in turn are the functions of thickness of film, refractive indices n_f, n_s, n_a, angle of incidence ϕ_a, wavelength of light. The separation of the equation into real and imaginary parts, yields one equation for (Δ) and another for (ψ). With two equations in hand only two unknown n_f, d_f one should be able to get both unknowns.

However the equations are very complicated and this is not possible analytically and numerical calculations by computer programming is essential.

A series of n_f are assumed for each of which

(Δ) and (Ψ) values are calculated for different values of film thicknesses d . Experimental values of (Δ) and (Ψ) $_f$ are interpolated compared with the corresponding computer calculated values to determine the unknown parameters n_f and d_f .

1.6.1 $\underline{(\Delta)}$ and $\underline{(\Psi)}$ MEASUREMENT THEORY.

The description of ellipsometer is given in chapter II.

The measurement theory, giving relation between (Δ), (Ψ) and actual angles measured P and A (i.e. polarizer angle P and analyzer angle A) are discussed in brief.

The azimuthal orientations of the polarizer (P) and the quarter wave plate (Q) determines the relative amplitudes and phase difference between the (p) and (s) components of the incident beam. These orientations are adjusted so that the differences in phase just compensates that which results from reflection, thus measuring (Δ). The plane-polarized,reflected beam is transmitted by the analyzer to a telescope and detector. When the above condi-tions of polarizer and quarterwave plate exists, the analyz-er (A) can be oriented to extinguish the reflected beam. This extinction setting measures (Ψ). The ellipsometric measuring technique interms of orientation of the polarizer, compensator and analyzer is shown in fig 1.6.1

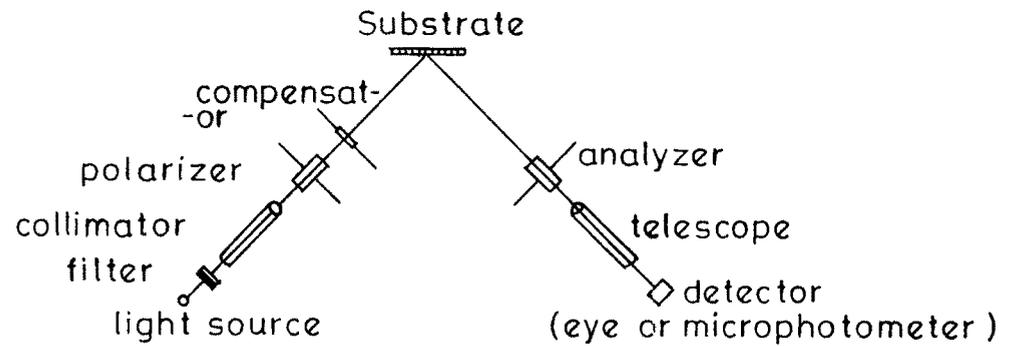The dependence of (Δ) and (Ψ) on the azimuthal orientation of polarizer (P), quarter-wave plate

Substrate

compensat-
-or

polarizer

collimator

filter

analyzer

telescope

detector

light source

(eye or microphotometer)

Fig. 1·6 — Schematic representation of gaertner Ellipsometer.

Incident beam

Polarizer

Mica wave plate

z

y

K

P_o

s

p

45°

Δ'

E_c

E_s

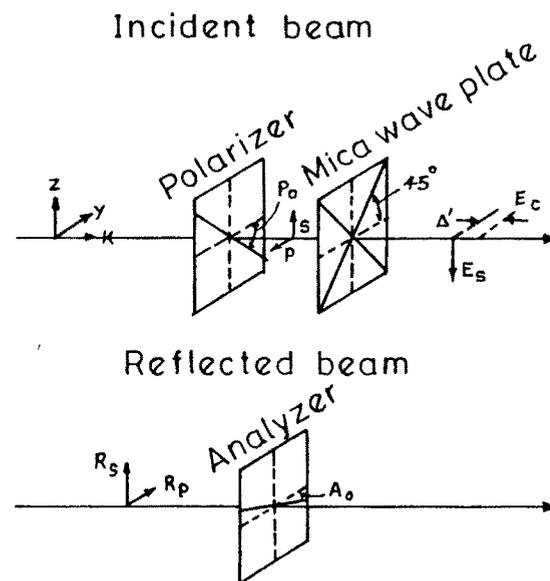Reflected beam

Analyzer

R_s

R_p

A_o

Fig. 1·6·1 — Representation of ellipsometric measuring
technique in terms of the orientations of
the polarizer compensator and analyzer
and the relationships between the p & s
components of the beam.

(Q) and analyzer (A) can be derived by a simple
       112
trigonometric relation.   Fig 1.6.1 shows the components

of the light beam after traveling through the compensator.

If Q is the azimuth of the fast axis of the

compensator, looking towards the source of light, P and A

are the polarizer and analyzer azimuths respectively,

and δ (normally about 90^0) the retardation of the wave

plate, the component of light along the fast axis of the

quarter wave plate is $\cos(Q-P) e^{i\delta}$ and along slow

axis $\sin(Q-P)$.

The expressions for the parallel and

perpendicular components of the electric vector after

transmission by the compensator are,

$$E^p = \cos(Q-P) e^{i\delta} \cos Q + \sin(Q-P) \sin Q \qquad 1.6.1.1$$

$$E^s = \cos(Q-P) e^{i\delta} \sin Q - \sin(Q-P) \cos Q \qquad 1.6.1.2$$

In the present case one of the azimuth i.e.
                                            o
Compensator is fixed at 45

Then,

$$\frac{E^p}{E^s} = \frac{1 + \cot(45 - p) e^{i\delta}}{-1 + \cot(45 - p) e^{i\delta}} \qquad 1.6.1.3$$

If the phase difference between the p and s

components of the incident beam (before reflection) is

defined as,

$$(\Delta_1) = (\beta^p - \beta^s) \text{ incident}$$

and if the ratio of amplitudes $(|E^p|) / (|E^s|)$ is defined as tan L, then

$$E^p / E^s = \tan L \ e^{i\Delta} \qquad 1.6.1.4$$

From equations (1.6.1.3) and (1.6.1.4) separating the real and imaginary parts one gets, [112]

$$\tan L \ \cos \Delta_1 = \frac{[\cot^2(45-P)-1]}{[\cot^2(45-P)+1-2\cot(45-P)\cos\delta]} \qquad 1.6.1.5$$

$$\tan L \ \sin \Delta_1 = \frac{[-2\cot(45-P)\sin\delta]}{[\cot^2(45-P)+1-2\cot(45-P)\cos\delta]} \qquad 1.6.1.6$$

which in turn yields

$$\tan (\Delta_1) = \sin \delta \tan (2P - 90^o)$$

for an ideal compensator $\delta = 90^o$

$$\sin \delta = 1$$

$$\tan (\Delta_1) = \tan (2P - 90^o)$$

$$(\Delta_1) = 2P - 90^o \qquad 1.6.1.7$$

From equations (1.6.1.3) and (1.6.1.4) the ratio of the amplitudes of the p and s components can be derived as ,

$$\cos 2L = - \cos \delta \cos 2P \qquad 1.6.1.8$$

When the polariser, quarter-wave plate and analyser are set for null position, the phase difference introduced by the film under study gets compensated by the phase difference Δ_1 introduced by the polariser and quarterwave plate and there are two 180° out of phase settings possible.

Thus for one extinction setting,

$$(\Delta) + (\Delta_1) = 0$$

i.e. $(\Delta) = 90^o - 2P$ 1.6.1.9

and for another extinction setting,

$$(\Delta) + (\Delta_1) = 180^o$$

$$(\Delta) = 270^o - 2P'$$ 1.6.1.10

Now the ratio of the amplitudes of reflected beam to the incident beam is denoted by equation

$$\tan(\Psi) = [\tan(\Psi_\gamma)] / [\tan(\Psi_i)]$$

$$\tan(\Psi) = [R_\alpha^p/R_\alpha^s] / [E_\alpha^p/E_\alpha^s]$$ 1.6.1.11

The plane polarised reflected beam will be extinguished when the analyser setting A satisfies

$$\tan(\Psi) = \cot L \tan(-A)$$ 1.6.1.12

Corresponding to polariser extinction setting P . If A' is the corresponding azimuth for P' the other possible alternative setting,

$$\tan(\Psi) = \cot L' \tan(A')$$ 1.6.1.13

where $L' = 90^o - L$

$$\cot L' = \tan L$$ 1.6.1.14

Therefore,

$$\tan^2(\Psi) = \tan(-A) \tan(A')$$ 1.6.1.15

Thus two positions of polariser settings P and P' corresponds to two positions of analyser settings A and A' to give minimum intensity.

If the compensator is a quarter wave plate $\delta = 90^0$ the relationships between (Δ), (ψ) and the extinction settings are

$$(\Delta) = 90^0 - 2P = 270^0 - 2P' \qquad 1.6.1.16$$

$$(\psi) = -A = A' \qquad 1.6.1.17$$

In order to select the correct equations for calculating (Δ) and (ψ), from a pair of extinction settings it is necessary to establish whether the settings correspond to equation 1.6.1.9 or equation 1.6.1.10. This is accomplished by noting that although (Δ) may have any value from 0^0 to 360^0, (ψ) is limited to values between 0^0 and 90^0. From this fact the sign of the analyser settings, according to equation 1.6.1.17 determines whether the setting corresponds to the primed or unprimed case.

Efforts are in progress to transfer the fortran IV computer programme[65] available for calculating refractive index and thickness to PC compatible programme. In this thesis only changes in terms of (Δ) and (ψ) are reported.

1.6.2 REVIEW OF SOME OF THE RECENT STUDIES ON EIIIPSOMETRIC TECHNIQUE

The ellipsometric technique mentioned in the previous section can be said to be the (Δ) - $\tan(\psi)$ method. It is basically a multimeasurement technique. This has been used in this work and also used by most of the workers in ellipsometry. The other type of ellipsometry is the

principle angle of incidence ellipsometry $\phi_p - \rho_p$ method. This method does not use a quarter-wave plate or any other compensator. Though this method is not a very popular one most probably because the measurement of angle of incidence is cumbersome. Various workers[113,114] have used the principle angle ellipsometry for finding thickness and refractive index of very thin surface films and is also very sensitive in detecting the optical anisotropy.[115]

In order to speed up the measurement time computer aided automatic ellipsometers have been designed and fabricated[116-119].

The monochromatic ellipsometer limits the interpretation of the characteristic of films. The optical analysis at any wavelength can be done by spectroscopic ellipsometer. Most of the instruments used light modulation method[118,120,121] for detection. A more improved version for insitu analysis[122] and dynamic imaginary micro-ellipsometry[123] have been developed. I An etal[124] have achieved submonolayer sensitivity using millisecond time scale. The spectroscopic ellipsometer has also been used at variable angle of incidence for characterisation of interfacial index gratient.[125,126]

1.7 AIM AND SCOPE OF THIS WORK.

As seen from section 1.4 not much work has been done on the properties of cerium oxide thin films. Most of the authors (sec 1.4) have studied the deposition aspects

of CeO_2 film and not on other properties and aging of these films. With this in view the mechanical and optical properties of vacuum evaporated cerium oxide films has been dealt with in this work. The technique of chopping[61,65-68] of the vapour flow during evaporation has been utilised here. The adhesion, stress and ellipsometric p arameters of (Δ) and (Ψ) have been measured for both nonchopped and chopped films. It has been found that chopped cerium oxide films shows higher adhesion, lesser stress and withstand better the ambient treatments of room temperature moisture, cold, moisture, salty moisture atmosphere and heat. Changes in (Δ) and (Ψ) were observed. By suitable control of various parameters of deposition and the rate of chopping, it is hoped to obtain a film with almost no aging effect, no stress and very high adhesion.

The details of experimentation is given in Chapter II. Chapter III gives the result of adhesion, stress and aging experiments on CeO_2 under the various ambients. Discussion and conclusion are presented in chapter IV.

Fig 2.2   THE VACUUM SYSTEM USED