CHAPTER - I

1.1 INTRODUCTION :

Application of thin films in various fields have made extremely rapid progress in recent years. The development of deposition technique for preparation of thin films with controlled and well defined properties plays an important role in technological applications.

Thin films can be regarded as matter uniformly distributed between parallel plates extended infinitely in two directions, the dimensions, however, of the material being constant and restricted along the third direction i.e. thickness. The thickness of thin film are usually less than 1μ (10,000 A°) for use in the visible range. A recent view point is that a film can be considered thick or thin depending on whether it exhibits surface like or bulk like properties.

Moisture plays a critical role in all aspects of thin film research. The knowledge of the ambient or controlled humidity levels is essential in order to properly account for the observed changes in the thin film properties with time.

Most of the day to day working of various industrial and technological process takes place under normal environmental conditions, where in moisture is a very

common component. The measurement and the control of this is very important.

1.2 CONCEPT OF HUMIDITY :

The relative humidity specifies the moisture level present in the atmosphere in terms of the maximum moisture (saturated vapour pressure) that can be present at the temperature of measurement. The knowledge of relative humidity would help in estimating the damage caused by the presence of moisture. Most of the effects due to moisture are due to the adsorption taking place on the surface of the thin film. The molecules on surface of solid are in a state of unsaturation, due to which they attract other molecules with which they come in contact and retain them in their surfaces. The phenomenon on the surface of solid is called adsorption.[1]

Two types of adsorptions i.e. physical and chemical adsorption are generally known. The force responsible for physical adsorption are the dispersive forces, where as in chemical adsorption the gas molecules combine with the surface to form a surface compound. Many cases of adsorption are a combination of both.

A feature of adsorption in porous solids is the presence of hysteresis during desorption and is shown in Fig.1.1. A schematic of adsorption and desorption is given in Fig. 1.2.

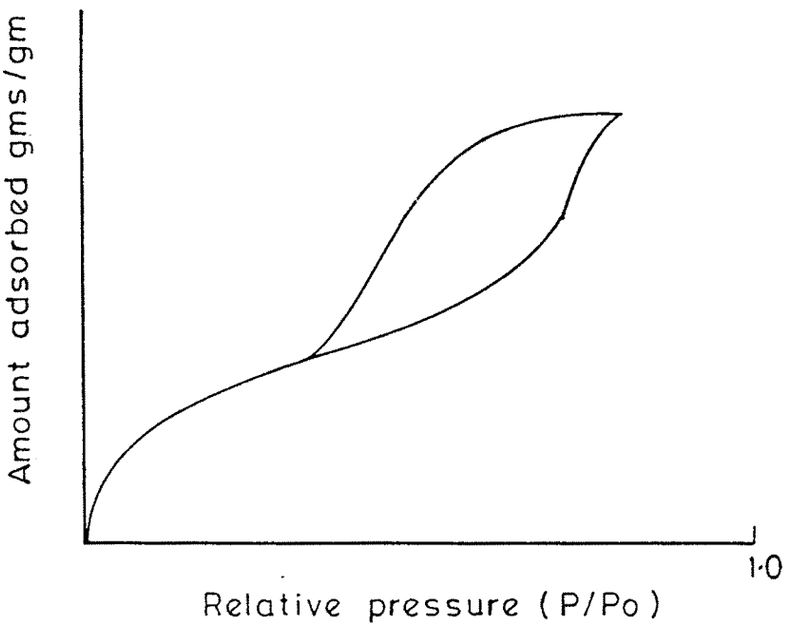


Fig. 1·1 - ADSORPTION OF MOISTURE ON SOLIDS.

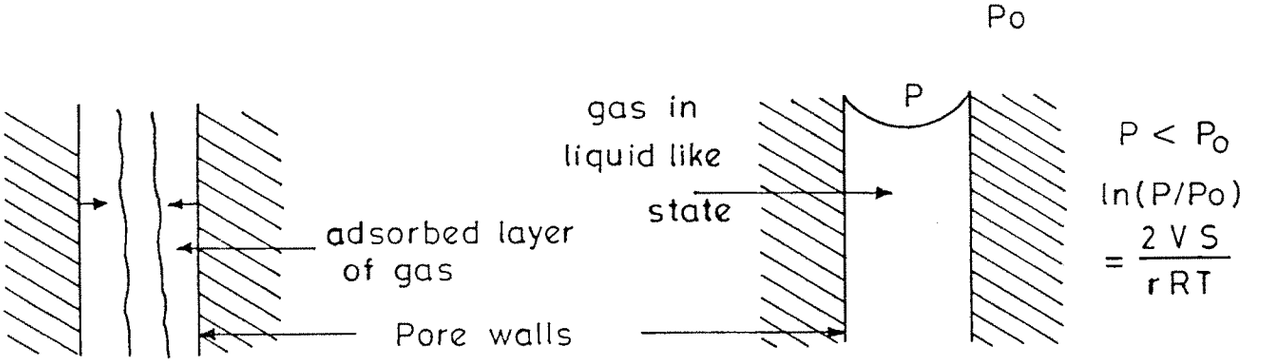


Fig. 1·2 - a) ADSORPTION PROCESS IN THE PORES OF A SOLID. ARROW INDICATES DIRECTION OF INC. IN THICKNESS WITH GAS PRESSURE.

b) DESORPTION PROCESS GOVERNED BY KELVINS EQUATION DUE TO FORMATION OF MENISCUS.

As shown in Fig.1.2, during adsorption the thickness of the adsorbed layer increases with incerase in moisture until near saturation when the layers from opposite walls coalesce and the pore is completely filled with the moisture in liquid like state. During desorption when the vapour pressure is reduced from the saturation vapour pressure, a meniscus is present over the adsorbed layer. As the moisture is having concave nature the vapour pressure just above the concave surface is less than the vapour pressure in the surrounding atmosphere. The Kelvin equation gives

$$\ln\frac{P}{P_o} = \frac{-2*V * s}{rRT}\cos\phi \quad \text{---------- 1.2.1}$$

Where P = Pressure over the concave surface

P_o = Saturated vapour pressure at T^oK

V = molar volume of the moisture in the liquid state

s = Surface tension

r = radius of curvature ofmeniscus

R = gas constant

ϕ = angle of contact

Due to this reduced vapour pressure, immediately, the liquid present in the pores does not evaporate until the outside vapour pressure is equal to or less than P. This effectively gives rise to the hysteresis of adsorption of porous solids.

1.2.1 POROSITY / PORE SIZE :

Adsorption is pronounced in the case of porous solids. Hence in the humidity sensor based on adsorption principle, a porous material would lead to greater humidity sensitivity.

As already mentioned porosity would result in hysteresis. So balance has to be obtained between porosity and hysteresis, so as to obtain a transducer with reasonable sensitivity, and minimum hysteresis. Hence porosity or pore size of the film which is used as the basic material for transducer would have to be determined. One of the method of determining pore size is by scanning electron microscopy (SEM). This enables direct evaluation of pore size, structure and distribution, from which porosity can be calculated.

Another method of evaluation of porosity is the packing fraction method. This method requires the knowledge of refractive index of the various materials involved.

The Lorentz-Lorenz formula[2,3] for the refractive index of the optically homogeneous mixture is

$$\frac{n_f^2 - 1}{n_f^2 + 1} = d_1 \frac{(n_1^2 - 1)}{(n_1^2 + 2)} + d_2 \frac{(n_2^2 - 1)}{(n_2^2 + 2)} + \cdots \quad \text{--------} \quad 1.2.2$$

Where n is the refractive index

n_f is refractive index of the film

n_1, n_2, n_3 are refractive indices of various components of mixture of which the film is made up.

d is the packing fraction.

Packing fraction is the ratio of volume actually occupied by material to the volume of the entire sample. So depending upon the type of material in the thin films, the equation can be simplified.

In the present case, assumption can be made that aluminium oxide film is a homogenous mixture of the oxide and air only. So the above equation becomes

$$\frac{n_f^2 - 1}{n_f^2 + 2} = d_m * \frac{n_m^2 - 1}{n_m^2 + 2} + d_m * \frac{n_{air}^2 - 1}{n_{air}^2 + 2} \quad \text{-------} \quad 1.2.3$$

As $n_{air} = 1$ the second term on right hand side is negligible. So packing density of material (d_m) is

$$dm = \frac{n_f^2 + 1}{n_f^2 + 2} * \frac{n_m^2 + 2}{n_m^2 - 1} \quad \text{----------} \quad 1.2.4$$

So to know d_m we should know n_f and n_m.

The porosity P can be evaluated as

$$P = 1 - d_m \quad \text{----------} \quad 1.2.5$$

1.3 MOISTURE SENSING DEVICES :

The oldest and basic form of humidity measurement

are the wet and dry bulb hygrometer and due point hygrometer. The first electrical hygrometer was described by Dunmore[4,5] which had Lithium chloride ($Licl_3$) as the sensing material. The variation in A.C. resistance with moisture was the measure of relative humidity.

1.3.1 ELECTRICAL HYGROMETER :

The basic principle behind humidity measurement is the variation of impedence due to moisture content. The electrical hygrometer can be classified in two categories.

First is the variation of resistance of hygroscope salts like $Licl_3$ and P_2O_5 and second is the resistance variation of porous dielectric with humidity.

The sensors with hygroscope materials are one time use sensors, where as the porous dielectric solid sensors can be reused after removing the adsorbed moisture.

1.3.2 SPECTROSCOPE HYGROMETER[6,7] :

In this type of instrument used for humidity measurement, one of the absorption bands of the water vapour spectrum in the UV or IR range is utilised to measure the water vapour density in air as the intensity of absorption is a function of the water vapour density.

Few advantages of this technique are

1) It has high sensitivity at low water vapour.

2) Fast speed of response of the order of one second

for all vapour pressure concentration.

3) Ability to effect air integrated humidity measurement.

1.3.3 HAIR HYGROMETER[8]:

Hair is cheap and strong and changes its length with humidity can drive the recorder pen or electrical switches. So hair actuated devices were in use in the form of recording hygrographs. The speed of response of hair to changes in humidity depends on temperature, stress on the hair and the direction of changes.[9]

Another type of hygrometer is Coulometric hygrometer.[10]

1.4 WORK DONE ON POROUS Al_2O_3 :

For many years the need for sensing humidity with low cost devices for both domestic and industrial applications has been deeply felt. Porous Al_2O_3 films are potential candidates for these type of sensors. The bulk of the literature available on these films are on anodic films on aluminium. There is no reference available for porous aluminium oxide obtained from oxidation of aluminium in steam environment and very few on oxidation by hot water. This article surveys the work done on porous Al_2O_3 films with specific reference to use as humidity sensing elements. Depending on the conditions, the product of the reaction

between aluminium and water vary. The composition of these films range from anhydrous oxide to trihydroxide. The product of aluminium oxidation in water is a poorly crystallised aluminium hydroxide, similar to boehimite. This product is some what porous[11,12].

According to some workers[13,14,15] aluminium oxide films formed by reaction with boiling water, one oxide phase is formed. The infra-red spectrum of these films showed a typical pseudo-boehimite.[16] The films formed at lower temperature (~ 40-60°C) are more porous as compared to those formed at 100°C .[16] If aluminium is oxidised with boiling water boehimite is formed.[17] The growth charactristic of Al_2O_3 films formed in distilled water at 58°C was studied by Ellipsometric technique by Phatak et al.[18] They have reported a linear growth rate of the oxide on aluminium in water at 58°C. Below 58°C the growth rate is slowed down after about 10-15 minutes. They conclude that probably 58°C is the critical temperature for thin films of aluminium obtained by vacuum evaporation.

The structure of anodic alumina films by infra-red spectroscopy technique have been studied by some workers.[15,19] Infra-red spectroscopy indicate that freshly prepared anodic film is a relatively open array of amorphous, largly anhydrous alumina crystallites, the surface of which carry hydroxyl group or ions. Studies on

porous anodic films on aluminium indicate that borate solutions, in the pH range 9-11 give less porous films.[20,21] Porous films obtained by anodic oxidation of aluminium in acidic electrolytes have unique structure composed of a packed array of columnar hexagonal cells having a cylindrical micro pore in the centre.[22,23] Furneaux et al[24] have succeded in forming porous Al_2O_3 with predetermined morphology.

Thin film barrier layer thickness had been measured for first time by O'Sullivan et al.[22] The morphology of the porous anodic oxide film under changing electrical and electrolytic conditions was also studied by electron microscopy. The mechanism of pore initiation in aluminium films have been investigated in details by many workers.[21,25-30] The regularity of pores was first determined by Booker et al[31] and minor changes in morphology by other workers.[32,33] The growth of the pores in a transition region barrier layer and the porous layer was conformed from infra-red studies by Dorsey.[34,35] He identified various absorption bands for different aluminas, as given below.

Alumina band type	cm^{-1}	Interpretation
1)AlO <— >H streach	3660-2940 cm^{-1}	Presence of H_2O. Free adsorbed or as hydroxide
2)Al<——>O	1696-1345 cm^{-1}	Monohydrate or anhydrous alumina
3)Al<——>OH	1162-900 cm^{-1}	Al hydroxide
	(1070 cm^{-1})	monohydrate
	(1025 cm^{-1})	Trihydrate

The use of anodized Al_2O_3 as capacitive humidity sensors was demonstrated by many workers.[37,38] Sato et al[39] have developed capacitive sensor on silicon substrate and on overlaying with 50 A° thick sputtered Al_2O_3, the hysteresis effect was reduced. A stabilising effect on the surface properties of hydrated Al_2O_3 layers was obtained by doping Al_2O_3 in different ion solutions.[40] Deposition on Si substrate was also done by R.K.Nahar et al[41] and Michel G. Kovac et al.[42] Electrical equivalent circuit model for Al_2O_3 humidity sensors has been proposed by some workers.[41-46] Resistive humidity sensors were studied by very few workers.[47-50]

A new type of electrical humidity sensor were developed by B.M.Kulwicki.[51] Application of porous Al_2O_3

films to surface acoustic wave humidity sensor is reported by Sato et al.[39] Use of porous Al_2O_3 films for multifunctional humidity / gas sensor has also been demonstrated.[52] Zhi Chen et al[53] have succceded in depositing porous Al_2O_3 through selective reactive evaporation method. Miniaturisation of Al_2O_3 moisture sensor to non destructively determined humidity levels inside sealed hybrid package was developed by Kovac et al.[42]

1.5 VACUUM TECHNIQUE FOR THIN FILM DEPOSITION :

Thin film deposition can be broadly classified as either physical or chemical. The schematic broad classification is given in Fig.1.5.[54]

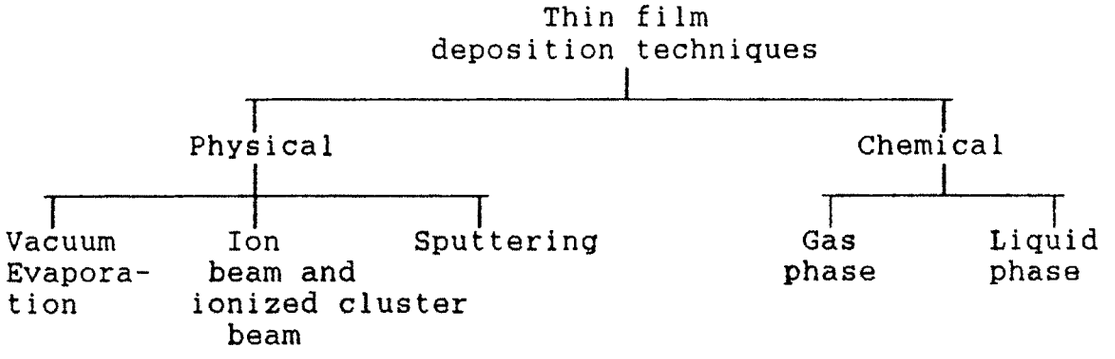


Fig. 1.5

1.5.1 PHYSICAL METHODS :

1.5.1.1 VACUUM EVAPORATION :

Vacuum evaporation although one of the oldest technique is still widly used both in laboratry and in

industry. It is a very simple and convinent technique. Excellent treatment of the subject of vacuum evaporation is given in Maissel and Glang.[55]

The basic steps involved in this are

a] Generation of the vapour from condensed phase solid or liquid

b] Transfer of the vapour from source to the substrate.

c] Condensation of the vapour on the substrate surface to form the solid film.

Different methods can be used for evaporating the material to be deposited.

1.5.1.1.1 RESISTIVE HEATING :

This is the simplest technique where the evaporation is done from a boat or a wire of a refractory metal eg. W,Ta,Mo, heated by electric current.

1.5.1.1.2 FLASH EVAPORATION :

In this method small quantities of the material to be evaporated is dropped on a hot boat for the material to be instantaneously evaporated. Stiochometric thin film of compound or alloy can be deposited by this.

1.5.1.1.3 ELECTRON BEAM BOMBARDMENT :

Is another method of accomplishing evaporation. A stream of accelerated electron is focused on the surface of the material kept in a water cooled crucible. The rate of

evaporation is significantly higher than the resistive heating.

1.5.1.1.4 LASER EVAPORATION :

Laser kept outside the vacuum system is used as a thermal source is focused on to the target material. The ejected material is deposited on the substrate kept in front of the target material inside the vacuum chamber.

1.5.1.2 SPUTTERING :

Bombardment of a surface with high velocity positive ions causes the surface atoms to be ejected.[56] This ejection of atom from the surface due to bombardment of positive ions usually inert is commonly known as cathode sputtering. When the ejected atoms are made to condense on a surface, thin film deposition takes place. The DC[57] and RF[58] glow discharge sputtering are the simplest and most commonly used. Triod sputtering, magnetron sputtering, ion beam sputtering are some of the other process available for film deposition.

Some other techniques which require high vacuum environment are ion plating, ion assisted deposition, molecular beam epitaxy, activated reactive evaporation.

1.5.2 CHEMICAL METHODS :

Another major technique for thin film formation is

the chemical process from gas or liquid phase. The most popular and important technique is the chemical vapour deposition.[59,60]

The constituents of the vapour phase react to form a solid film on the substrate surface, which is maintained at a suitable temperature. To activate the chemical reaction laser source, photons or plasma can also be used.

Another simple chemical method is the electro-deposition which is an electro-chemical process in which the anode and cathode (cathode being the substrate) are immersed in a electrolyte and electric current passed . The thin film is deposited on the cathode.

Anodisation is another electro-chemical process, reaction taking place at the anode. When an electric current is passed, an oxide coating forms on the surface of the metallic anode. That is the anode reacts with the negative ions from the electrolyte and forms an oxide coating. aluminium is one of the few metals that gives useful films by this simple method.

Electroless deposition is a film deposition process in which no electrode potential is applied, unlike electro-deposition. This technique is simple and with this large area deposition is possible.

1.6 REFRACTIVE INDEX :

Refractive index is formally as the ratio of velocities.Mathematically it is represented as sin i /sin r. There are various methods available for measuring refractive index.Table 1.6 gives the various methods.[61]

The most simplest and oldest method is due to Newton and later modified by Vasicek[62], where in the interfrence colours were used to obtain the refractive index after knowing the metric thickness and angle of incidence.The Brewester angle method is also known as Abele's method is used in this work to find refractive index. The theory of this technique is given in brief.

Abele's Method :-

It is a simple and accurate method to find refractive index. This is used for those films whose optical thickness lies in the neighbourhood of odd multiplies of quarter wave length and film refractive index is not far off from that of substrate. Here a spectrometer with a scale which can read to one minute of arc is required. At an angle of incidence ϕ_A = arc tan (n_1/n_2), the reflectance of the P component of an incident light beam is the same over a film covered surface as that over substrate. The film refractive index being n_1 and n_2 is the refractive index of medium of incidence generally air. Near this point in the reflectance curve, the slope of the curve for various thickness are

Table 1.6

Various Method of Refractive Index Measurement

Method	Suitable	Accuracy	Remarks
Reflected colour	n,t	± 10%	The range is $\lambda/4$. Suitable for few λ. Requires transparent substrate.
Reflectance at different wavelengths	n,t	variable	Useful for few 100 Å thickness to several wavelength. Entails absolute reflectance measurement
Michelson Interfero-meter	n,t	± 0.003	Used for thickness from 100 Å to several hundred wavelength.
Brewester angle	n,t	± 0.002	Difference of the refractive index of substrate & film not>0.3.
Polarimetric	n,t	± 0.0005	Computerisation lengthy.
Ellipsometer	n,t	± 0.0001	Effect of polarisation produced by reflection on sample surface is measured. Needs computer programming and data processing.
Wave guide	n		The limitations are the substrate refractive index lower than film index and coupling prism greater than film index.
Envelope	n		Sensitive to film thickness non-uniformly and substrate non-uniformly.

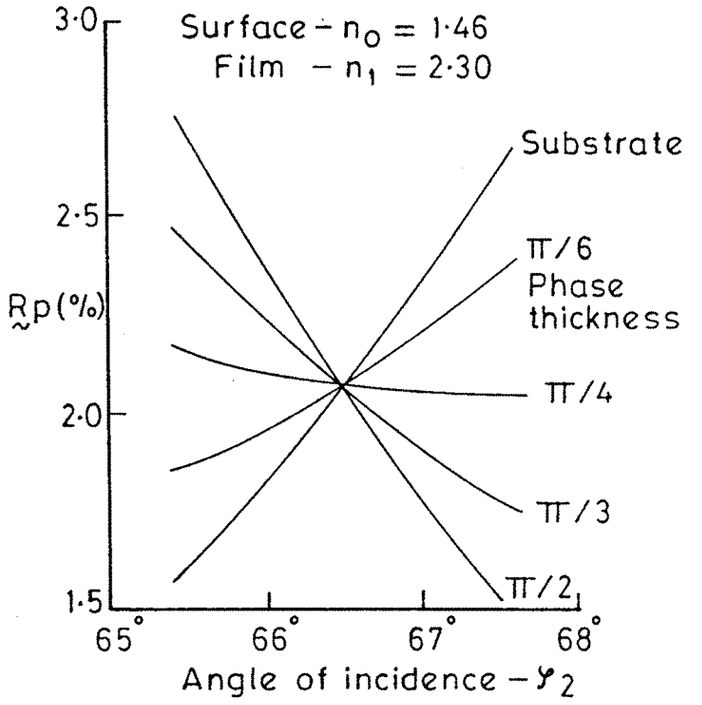


Fig. 1·6 – VARIATION OF R WITH ANGLE OF INCIDENCE FOR SUBSTRATE AND FOR FILMS OF VARIOUS THICKNESS.

shown in Fig. 1.6[63].

For films of optical thickness equal to even multiple of $\lambda/4$, the reflectance curve is almost, but not quite same as that of bare substrate. For an optical path difference of integer $\lambda/2$, The optical parameter are precisely same as that of the substrate.

The path difference will vary with the direction of beam so, a given film satisfies this condition for only one angle of incidence. This condition of equal reflectance of film and that of substrate is on the assumption that film shows no absorption.

1.7 ADHESION :

From the point of view of sensors which have to undergo physical/chemical transformation repeatedly during their operation, the adhesion of the thin films coating acting as the sensor element is of great importance. Adhesion is defined as the work necessary to seperate the coating substrate interface.

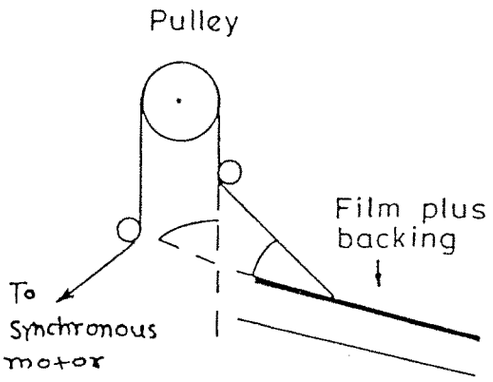
Adhesion of thin films is influenced by a number of parameter, like the choice of coating and substrate material, substrate preparation, coating method, composition of residual gas at the substrate surface and stability of film substrate system.[64]

Table 1.7 gives the various methods of measuring adhesion and Fig.1.7 depicts some of the common methods of

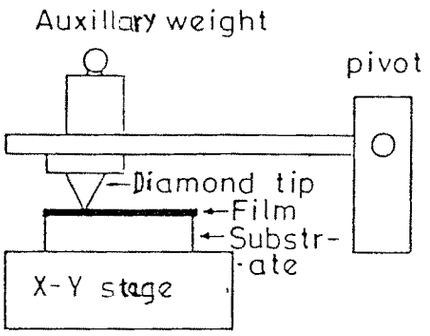
TABLE 1.7

METHODS OF ADHESION MEASUREMENTS

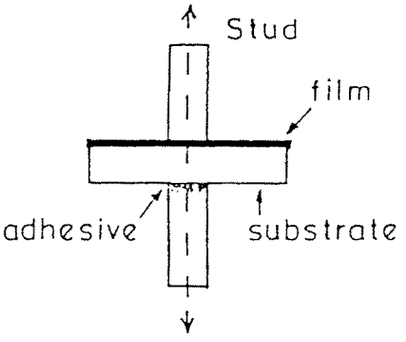
Qualitative	Quantitative
Mechanical Method	
Scotch tape test	Direct pull-off method
Abrasion test	Moment or topple test
Bend or Stretch test	Ultracentrifuge test
Shearing Stress test	Ultrasonic test
	Peeling test
	Tangential shear test
	Scratch test
Non-mechanical Method	
X-ray diffraction	Thermal method
	Capacity test
	Nucleation test



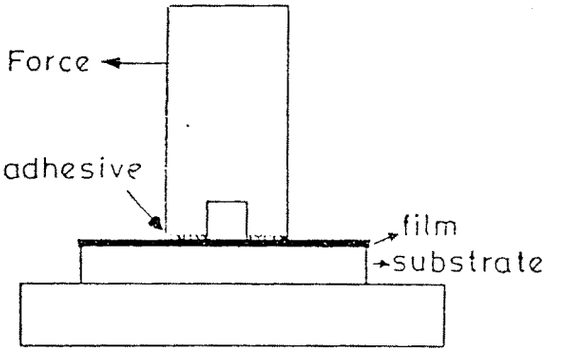
(a) The peel test



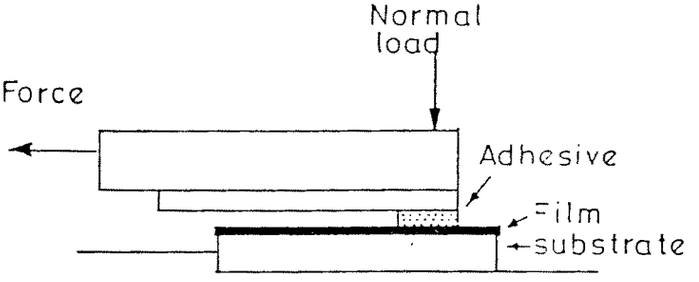
(b) Schematic of the scratch test.



(c) The direct pull off method



(d) The topple method



(e) The tangential shear test

Fig. 1.7 – Methods of adhesion measurement.

adhesion measurement.

1.7.1 SCOTCH TAPE METHOD :

Strong[65] originally used this method. His experiment consists of a smooth round chrome steel point across a film surface. A gradually increasing vertical load was applied till a channel was formed for a particular load. A critical load at which clean tracks were visible under a microscope, was taken as measure of adhesion.

1.7.2 ABRASION METHOD:

In this method the film is abraded by either energy loaded rubber or by stream of fine silicon carbide particles.[66] The removal of film is measured by measure of electrical resistance of the film. The time of abrasion can be related to adhesion.

1.7.3 DIRECT PULL OFF (DPO) METHOD :

The fracture at the film substrate interface[67] is measured from force per unit area exerted by a pulling device in a perpendicular direction attached to the film. Since this method is used in this work the other details of the method will be given in chapter II.

1.7.4 MOMENT OR TOPPLE METHOD :

Here the force is applied in the horizontal direction and the moment of the force required to break the film from the substrate is a measure of adhesion.[68]

1.7.5 ULTRA CENTRIFUGAL METHOD :

In this method the films are uniformly deposited into a cylindrical surface of small stainless steel / rotors of approx. 0.1 inch diameter. These rotors are magnetically suspended in vacuum and spun and higher and higher speeds untill the film is thrown out. In this method no adhesive or solder is used.

1.8 ELECTRICAL RESISTANCE :

Various mechanisms exists to explain the transport phenomenon especially in amorphous films. The analysis of experimental data is complicated and fraught with uncertainity because a number of these mechanisms may operate simultaneously in a practical thin film.

To the authors knowledge only one report[69] on planer resistors made of AlO-x thin films is available. The resistivity measurement method covers the entire range of contact and non-contact approach by different workers.[37,70,71]

The mechanism of charge conduction through thin Al_2O_3 films sandwiched between two electrodes has been a topic of intensive theoretical and experimental study[72-75]. Khanna et al[76] have proposed a two carrier mechanism to describe charge transport on porous Al_2O_3.

The humidity sensitive electrical properties of porous Al_2O_3 films have been investigated by various workers.[42,44,77,78]

1.9 IR AND XRD SPECTROSCOPY :

Infra-red spectroscopy is the most widely used analytical tool for determination of moisture in porous films. Bernald et al[11] have reported that the films formed on aluminium immersed in boiling water consists of hydrate of aluminium oxide containing upto 32% of water.

It is reported[16] that absorption bands of aluminium hydroxide occured in three ranges, 3000-3700 cm^{-1} corresponding to band AlO-H stretch, 1300-1700 cm^{-1} corresponding to HOH bend and 800-1200 cm^{-1} corresponding to Al-OH bend.

Comparison of IR spectra of aluminium oxidation in water and anodic Al_2O_3 was made by Vedder et al[79] and they discussed the peaks obtained in the range 800-4000 cm^{-1}

O'Sullivan et al[15] studied the hydrothermally treated anodic alumina films by IR spectroscopy, of freshly prepared films under ambient conditions at moisture absorption band 1640 cm^{-1} wave number and stretching mode of hydroxyl species between ~ 700-3700 cm^{-1} wave number. The report on IR studies on water containing glass was made by R.F.Bartholomew et al.[80]

Few authors[81-83] have used X-ray technique to investigate the formation of Boehimite by putting the aluminium in boiling water.

1.10 AIM AND SCOPE OF PRESENT WORK :

As indicated in Article 1.1 moisture plays a critical role in the performance of electronic devices, and thin films. This moisture effect was studied in our lab. with respect to optical films[84-87] of ZnS, MgF_2, CeO_2. Most of the reports are on porous Al_2O_3 films obtained by anodic oxidation. Very few work is available on hot water oxidised films and almost no report is available for steam oxidised Al_2O_3 films. Most of the reports[37-43] are on sensors in capacitor form.

The present work reports the humidity sensitive characteristics of aluminium oxide monohydrate ($Al_2O_3 \cdot H_2O$) obtained by oxidation of evaporated aluminium films in water at 60°C and by passage of steam over the film. To the aurhors knowledge there are no reports on the oxidation of Al by steam to obtain porous Al_2O_3. Also there are no studies on adhesion of these films. The adhesion of both the types of films were also measured. The refractive index/porosity of these films have been studied by Abele's method and the cyclic changes in heat moisture cycle has been reported for both the types of Al_2O_3 films. DC resistance variation of these film with humidity has also

been reported. Infrared spectroscopy studies were carried out to determine the moisture absorption band and from that determine the sensitivity of the sensor to moisture.

The humidity sensors reported are of high thickness (>0.5 μ). One of the aims of this work is to tailor the pore distribution by means of steam oxidation of Al to obtain low thickness (< 2000 A°) Al_2O_3 films with very good adhesion and response charactristic comparable with other Al_2O_3 sensors. The success in this endevour is given in chapter III.

The experimental procedure has been given in the chapter II, and results and dicussion in the chapter III and IV respectively.

Importance :

Indegenisation of technology and materials, has been the need of the time in India. This requirement has initiated the efforts needed for actual development and fabrication of a humidity sensing system along with the basic research required for characterising various humidity sensitive materials.

Humidity sensors have wide spread applications ranging from domestic applicances, automobiles, medical sciences,process industries,agriculture and materology. The ability to design porous films of predetermined morphology makes them potentially well suited for the use as porous

membranes. At present humidity sensors are discrete components. When large scale application develop, integration of the sensors with the component will be cost effective.