Deposition & Characterization of Various Types of Coatings by Thermal Evaporation Method

Aditya Vamshi Basa [1], K.Venu [2], Godisela Ram Murthy[3] T.Aruna Kumari[4]
[1]A.V.College, Osmania University, Hyderabad
[2]Department Of Geophysics, Osmania University, Hyderabad
[3]Department of Applied Physics, National Institute of Technology, Kurukshetra
[4]Department of Physics, SRI SAI Degree & P.G.College, Osmania University, Hyderabad
Email - venugeophysics@gmail.com

Abstract: *The objective of the work was to study and learn about the thin film coatings design and development of various types of coatings. The study of various thin film coatings helped in the development of Humidity sensors. The development of these sensors depended basically on the change in resistance of TiO2. Films with respect to humidity. In the first chapter the description is about the background of thin films i.e. how the thin films were developed, their concepts and design of thin film coatings.In second chapter physical vapor deposition techniques i.e. thermal evaporation method, electron beam gun for thin film coatings have been discussed. Feasibility studies for development of Humidity sensor and their characterization in third chapter. In the last chapter described about meteorology and applications of the thin films*

Key Words: *film coatings, Humidity sensor, vapour, vacuum.*

1. INTRODUCTION:

Thin films are deposited on to bulk materials (any substrate) to achieve properties which are unattainable or not easily attainable in the substrates alone. Thin solid films of metals, dielectrics, semiconductors and combinations of these in the thickness range few angstroms (1A=10^{-10} m) to microns (1micron= 10^{-6} m) deposited on metallic and non-metallic substrates find enormous and diverse applications in science and technology.

In the present state of science and technology, thin films play an important role in the investigations of the fundamental properties of solids and in revolutionizing the basic concepts, quality and performance of science-based industrial products. In fact, they have crossed the frontiers of laboratory investigations and become the backbone of present-day electronic, optical and automotive industries as well as playing a pivotal role in the harnessing of solar energy. Thin films have pervaded almost all branches of investigations and characterization of the fundamental properties of solids. They have been commercially exploited with great success in the development of such devices as thin film transistors, resistors, capacitors, memory elements of computers, optical interference coatings and devices, amorphous silicon solar cells, as well as various types of sensors to detect gasses. Their superior performance as regards sensitivity, reliability and stability is well established.

In recent years, thin film science has grown worldwide into a major research area. The importance of coatings and the synthesis of new materials for industry have resulted in a tremendous increase of innovative thin film processing technologies. Currently, this development goes hand-in-hand with the explosion of scientific and technological breakthrough in microelectronics, optics and nanotechnology. These films are essential for a multitude of production areas, such as thermal barrier and wear protections, enhancing service life of tools and to protect materials against thermal and atmospheric influences. Here we concentrated only on optical thin films (www.google.com[11]).

In this, first we explained the design of thin film coatings and thermal evaporation coating plant. In the second part we described how we deposited the films using thermal evaporation technique. and deposition of Tio_2 film for humidity sensor Finally we characterized those films using spectrophotometer. Tio_2 film characterized by spectrophotometer, Ellipsometer and atomic force microscopy

2. METHODOLOGY:

- A thin film has its dimensions in macroscopic scale only in length and Breadth. Its thickness is negligibly small (few microns or less) which gives the interference effect.
- These Thin films are used to manipulate or tailor make the optical properties of Transmittance, Reflectance and Absorbance of an optical component.

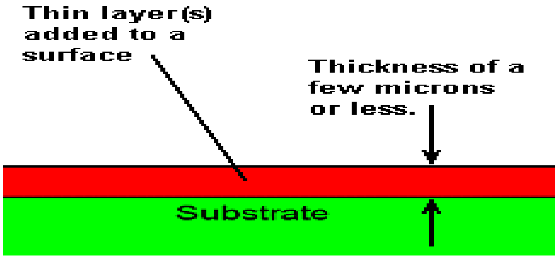


Fig. 1

An optical thin film may be regarded as one whose thickness is of the order of wavelength of the light interacting with it. This implies that a film of some material of thickness say 100 microns can be regarded as a thin film with infrared light (wavelengths few microns to several tens of microns),but if it interacts with ultraviolet light (wavelengths less than 0.3 microns) this film cannot be regarded as a thin film (Ronald R.Willey[1]).

Thin film optical coatings play a very important role in all type of optical instruments used in scientific research and industrial applications. Today, there is no optical instrument, even the most simple, which does not have optical coatings on the surfaces of the optical elements like lenses, prisms, mirrors used in the instruments. The purpose of optical coatings is to change, to a desired extent the optical characteristics of surface being coated. There are different types of optical coatings e.g. high reflectance coatings, anti reflectance coatings, interference filters, beam splitters etc

3. THERMAL EVAPORATION:

The thermal evaporation is the one of the methods of PVD. This method is normally used for low melting point materials examples are Al. Ag , Au, Sio,Mgf2. The details are described below.

3.1 VACUUM CHAMBER:

The chamber is fabricated from polished stainless steel. Two circular glass windows permit visual inspection of the coating process. The chamber is raised from the base plate by means of hydraulic pump. When required the chamber can be lowered by electro magnetically operated valve which opens an orifice and allows the hydraulic oil to be returned to the oil reservoir. When lowered the chamber makes a vacuum tight seal with the base by means of an "L" type neo-prene gasket. A micro switch at the top of the hoist cylinder automatically prevents the chamber rising above a preset limit. To provide clear space for the operator during loading operations the chamber, when raised, can be swung towards the rear after removal of the securing pin (www.wikipedia.com[12]).

Cooling water pipeline is attached to the outside of the chamber prevent over heating especially at the chamber windows. At the top of the chamber provision is made for the entry of a centrally positioned shaft seal for rotary work holder drive.

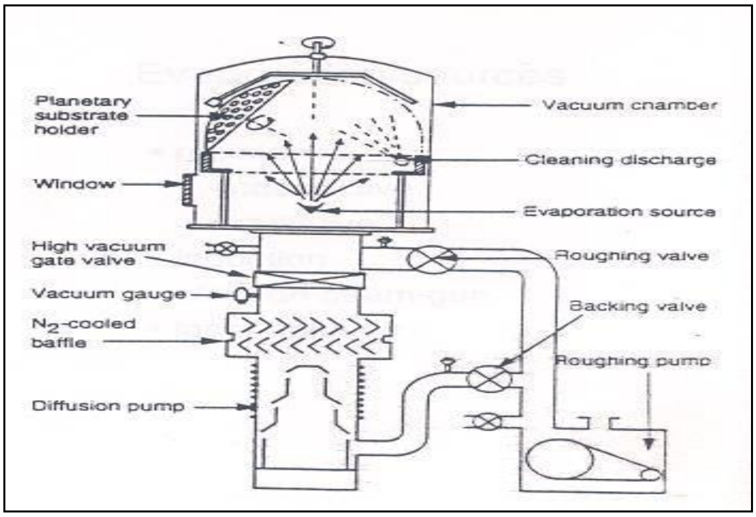


Fig 2 Vacuum coating plant with thermal evaporation source

The shaft is vacuum sealed by means of a Wilson seal and one side is connected to a reduction gear box and other side to a lever to rotate the rotary mechanism. Two valves are fitted to a chamber body one for admitting air quickly into the chamber at the end of the coating cycle, the other a fine control needle valve for admitting controlled flow of air or gas into the chamber during H.T. discharge cleaning.

3.2 VACUUM PUMPS

i) Why vacuum

- High chemical purity.
- Good adhesion between the thin film and substrate.
- Control over mechanical stress in the film.
- Deposition of very thin layers, and multiple layers of different materials.

In thermal coating plant at CSIO we are using two pumps for acquiring high vacuum.

a) Rotary pump b) Oil diffusion pump

Rotary pump Working:

Rotary pump involve three basic steps to create a vacuum. These are air trapping, compression, and outlet. In this rotary pump inlet dimension is greater than the outlet dimensions to compress the air.

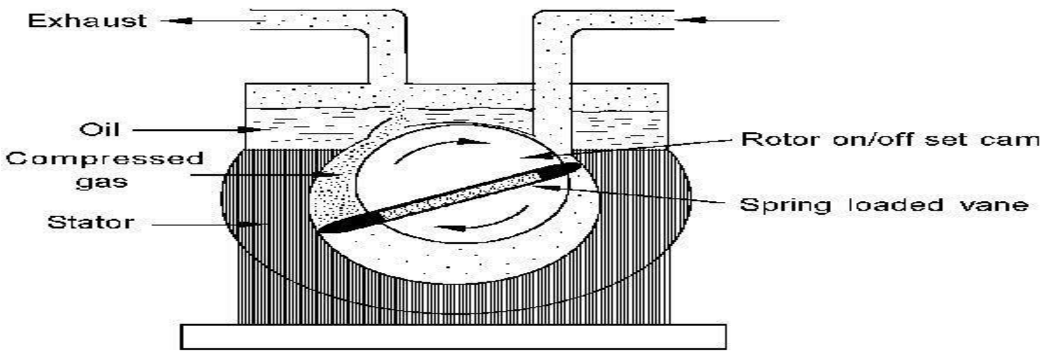


Fig 3

And the second step consists of stator and rotor. Stator is unmovable and rotor is moving inside the stator by some mechanism. And rotor consists of two vanes to sweep inside the stator .basically when the air coming to the system then the one side of vane is closed so that the air is trapped. By rotating the rotor It will go toward the outlet so that while compressing taken amount from the inlet will goes to outside through the outlet. At the outlet side there is valve to exhaust the air. It will open when the pressure is at the outlet greater than the atmosphere. Sometime due to this reason air will not go outside through the outlet. So we are using gas ballistic pump to give the additional amount of air pressure. On the outlet valve oil is there because after create a vacuum outside air is not entered into the system. The rotary pump creates the vacuum up to the 10^-3 torr.

Diffusion pump: Oil diffusion pump:

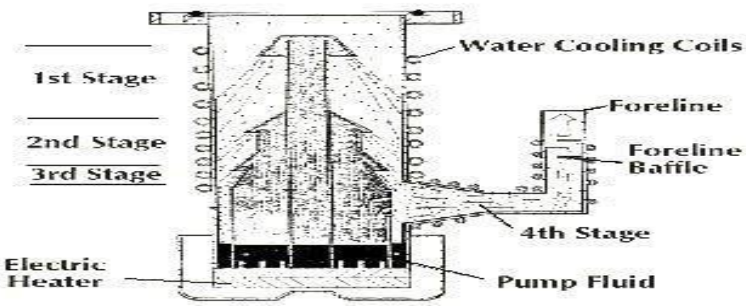


Fig.4 Oil Diffusion pump

Principle and Working: It can be used to create a high vacuum (10-2 to 10-6) torr due to sucking the vapors in the chamber by heating the oil in the boiler at the bottom.

When the pump fluid in the boiler is heated, it generates a boiler pressure of a few torr within the jet assembly. High-velocity vapor streams emerge from the jet assembly, impinge and condense on the water or air-cooled pump walls, and return to the boiler. In normal operation part of any gas arriving at the inlet jet is entrained, compressed, and transferred to the next stage. This process is repeated until the gas is removed by the mechanical fore pump (H.A. Macleod[2]). This pump is widely used for achieving high vacuum in thin-film evaporation units (Radio frequency sputtering).

Vacuum gauges:

Some of the general vacuum gauges we are going to discuss .pirani hot wire gauge for measuring the gas pressure doing rough pumping and when the backing diffusion pump. Basically we are using pirani gauge and penning gauge.

pirani gauge:

A gauge is constructed by the pirani is one of the most widely used .vacuum instruments it consist of glass or metal envelop containing a heated filament of metal with a high temperature coefficients of resistance ,such as platinum or tungsten.

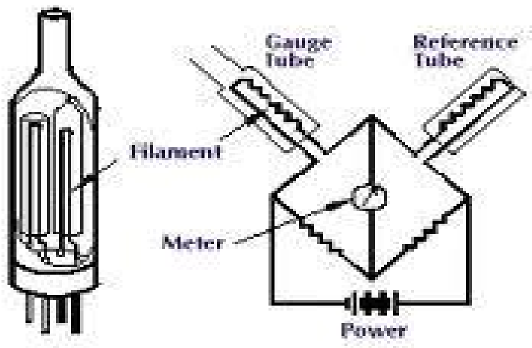


Fig 5

As the pressure in the gauge tube increases, the temperature of the filament and therefore its electrical resistance tend to decrease .The usual control circuit for a pirani gauge is Wheatstone bridge .In which one leg of the bridge is filament of the gauge tube is different, and the other legs have nearly resistance equal .The resistance convert into the pressure. It can measure 760 torr to 10^-3 torr .

Penning gauge:

These gauges are used to 10^-2up to 10^-6 torr it can measure. the useful life of hot cathode ionization gauges is determined by that of the incandescent cathode ,which is very sensitive to chemical attack ,and bombardment of positive ions. two parallel connected cathodes are used and midway between them is placed the anode the cathodes are metal plates .which the anode is a loop of metal wire whose plane is parallel to that of cathode .A potential difference of about 2kv maintained between and cathode. In addition a magnetic field of order of 500 oersted is applied right angles to the plane of electrodes by permanent magnet.

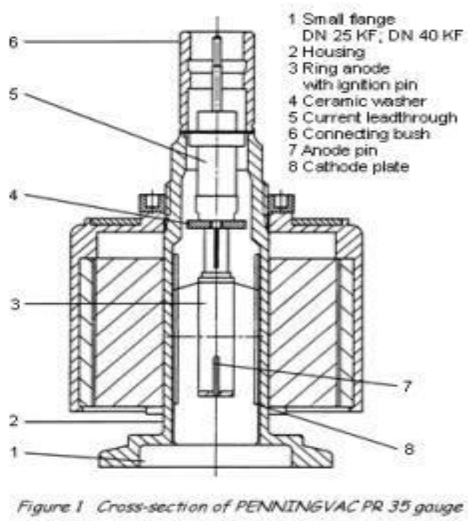


Figure 1 Cross-section of PENNINGVAC PR 35 gauge

Fig 6

An electron emitted by the cathode is accereleted towards the anode by electric field, but the action of the magnetic field causes its path to be in form of helix. The electron generally passes through the plane of the anode loop until its path is reversal by the electric field due to second cathode. The electron continues to oscillate in the manner about the plane of anode loop, due to the very long path of electron the ionization probability is high even low pressure. The positive ions created are captured by the cathode, produces ion current in the electrical circuits.

3.3 VACUUM VALVES:

The system contains the following vacuum valves

- The hand operated water cooled baffle valve is fitted to the 21" dia. Stainless steel base plate. This valve isolates the chamber can be brought into atmospheric pressure with out switching off the pumping system (High vacuum Technology[4]).
- Two numbers of 1" quarter swing butterfly type pipeline valves are fitted one in the backing line and the other in the roughing line.
- A quarter inch air admittance valve is fitted to the chamber to release the chamber vacuum after coating process.
- Rotary air admittance valve, it is used for exhaust and enter the gas when switch off and on the system. Its main purpose is to avoid the oil rushing into the pipeline.

3.4 ELECTRICAL SUPPLIES

- The L.T. supply for evaporation filaments or boats is obtained from a 230V input transformer by means of parallel or series connections in the secondary of the transformer.
- The H.T. supply for glow discharge cleaning (ion bombardment) is obtained from a high reactance transformer rated 3.5 KV@500 mA 5 KV. Open circuit.
- The input voltage to the L.T. and H.T. transformers is first selected on a rotary switch on the electrical control panel and then fed to a manually operated "Variac" variable transformer.

3.5 EVAPORATION SOURCE

A thermal evaporation system which consists of a four position vapour source turret constructed in copper permitting current loading up to 400 Amps is used. The heavy low tension and earth brushes are in permanent contact with rims of the turret low tension and earth plates for smooth arc free operation. The turret which is supported on a circular plate positioned above the base plate is rotated by an external hand wheel. The movement is transmitted into the vacuum system via a 12 mm Wilson shaft seal and a chain drive. The evaporation is carried out from the vapour source positioned vertically below the periphery of the work holder ring. Each source is positively registered into the evaporation position by an evaporation source lock lever and numbers indicate which source is in position. Apply L.T. to the indicating source, and vary the current through rotating the varic, then slowly evaporate the material.

3.6 RESISTANCE SOURCE

To bring the coating material to evaporation temperatures have been resistance sources. These sources are made of tungsten, tantalum and molybdenum etc. it holds the material to be evaporated and is heated by passing a large electrical current through it. Some of the resistance sources shown below.

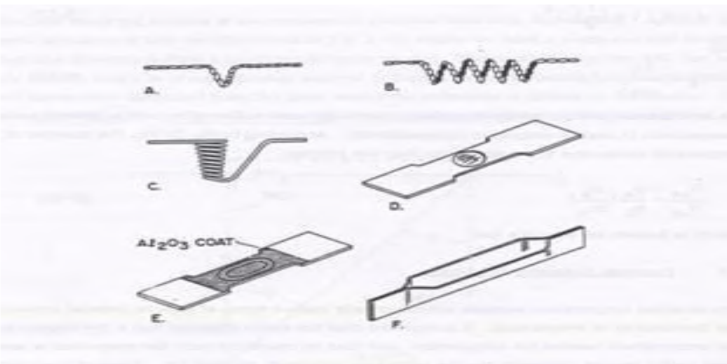


Fig. 7 Resistance Sources

A. Hairpin sources types B. Wire helix type C. Conical basket type (tungsten coil)
D. Dimpled foil type E. Dimpled foil with oxide (molybdenum or tantalum)
These boats (D, E, and F) are used for the materials like oxides evaporation.

3.7 WATER COOLING

Cooling water at 15ºC

Consumption: 6 liters /minute

Cooling water pipeline is attached to the outside of the chamber prevent over heating especially at the chamber windows and also diffusion pump.

3.8 E-B GUN EVAPORATION

In high vacuum coating plant (PLS-570), E-B gun used as evaporation source for evaporating material, turbo molecular pump used for high vacuum i.e., 10^{-7} torr, Quartz crystals are used to monitor deposition rates (thickness monitoring).

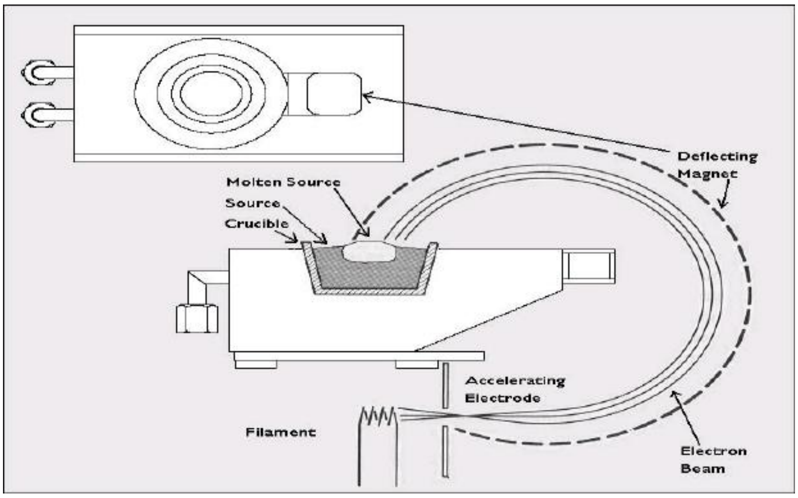


Fig.8

Mainly oxide films can be developed by using high vacuum coating plant. Such as SiO2 ,ZrO2 ,TiO2. It is used for oxides because these are having high melting point. Such as SiO2,ZrO2,TiO2.

In this plant, we can get hard coatings and thickness in range of nanometers.

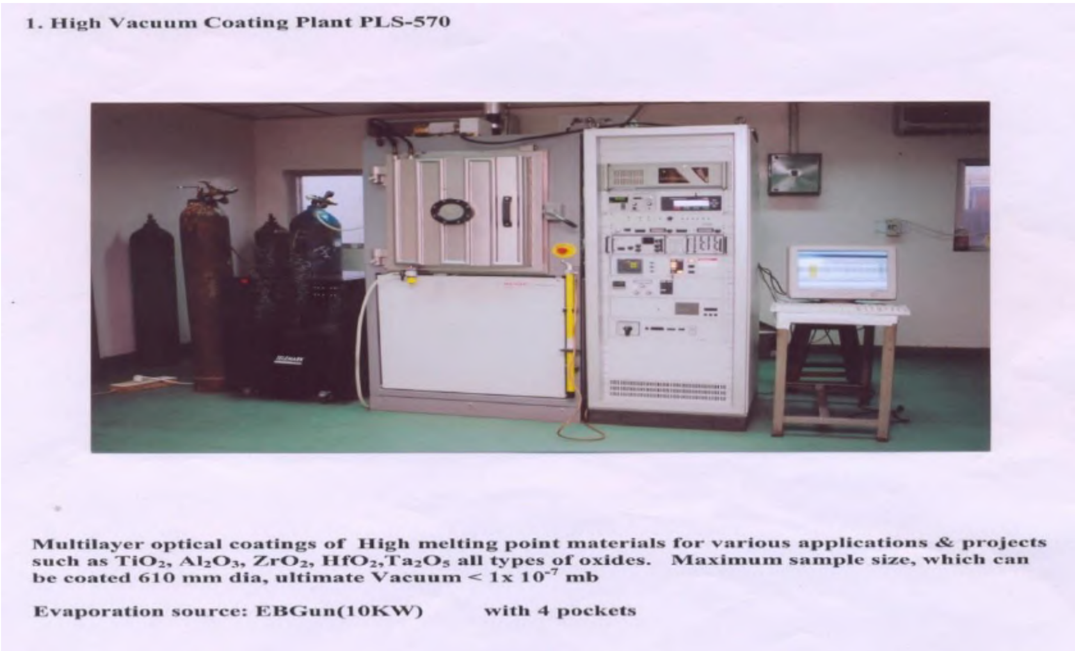


Fig.9

Mostly every material can evaporate through E-B gun. Plant contained the automatic shatter, cooling monitor, electronic drive unit, pumping unit control, vacuum monitor, high voltage control unit, pumping station and glow discharge unit etc. these all operations can do manually or automatically. At that time we can use four different materials with four pockets. In this plant, multilayer coatings can do with high accuracy.

Crystal oscillator:

Crystal oscillator is used to measure the thickness of the coated material, how much thickness will be on substrate It is placed at the chamber .In the evaporation process some of the material also fall on the quartz crystal, than the oscillator of crystal is reduced due to the mass. Then the changes in the frequency it will show the appropriate thickness

3.9 HUMIDITY SENSOR

Humidity plays a very important role in human life. Therefore monitoring and control of humidity is essential in various fields and instruments. Depending on the need, humidity sensing has been carried out by different kinds of sensors humidity sensors requires high sensitivity.

Therefore there is an increasing need to develop a cheap and highly sensitive electronic humidity sensor. We used TiO_2 film as a humidity sensor. TiO_2 films have excellent properties i.e. high optical transmittance in visible and IR region, high IR and better durability which is suitable for humidity sensor applications Tio_2 has a high capacity for adsorption of water molecules due to its porosity which is easily controlled (Vacuum engineering[9]).

Its amorphous structure is transferred into more stable rutile structure at appropriate temperature. The sensing element of the humidity sensor here consists of rutile structure. Ti (Titanium) thin film is deposited on the glass substrate which is further heated in a furnace at different temperatures for getting various structures. The TiO_2 film so developed has the rutile structure and porosity which helps in achieving rapid response and measures the humidity from 6% to 70%.

Response time= $\sqrt{t}$

Where t is thickness of the film

Response time of sensor is in milliseconds

Using PVD Tech we can achieve the low response time than the CVD Tech.

Pure Ti film has hexagonal structure

Tio2 exist the four structures

- amorphous
- anatase
- Brokite
- Rutile

These structures depend on the annealing temperature and time of annealing after the deposition of Ti film. TiO2 films are highly adhesive to glass surface posses exceptional abrasion and chemical resistance and have fairly high refractive index in visible and IR region.

After deposition of Ti on glass substrate at $4*10^{-5}$ torr. It is tempered in air , the metal film is completely oxidized to tio2. Before heating the Ti has hexagonal structure and tio_2 at low temperature has amorphous structure after heating the tio2 coated sample at 350 for 3hrs the tio_2 transforms into more stable rutile structure and porous structure which is sensible to humidity (James D. Rancourt [3])

The main principle is Change in TiO_2 film resistance according to relative humidity While increasing relative humidity the film resistance will decrease due to conductance of the TiO_2 film

When heating the film the crystallinety increases with the temperature.

$$\text{Sensing (s)} = \frac{change\ in\ resistance}{corresponding\ change\ in\ RH\%}$$

RH: dimensionless quantity

After heating the sample the sample refractive index, thickness and transmittance increases due to the rutile structure Before heat treatment the film atoms has zigzag position (Hexagonal Structure)

That rutile structure gives the increase in transmission, refractive index and thickness as compare to the Ti (Hexagonal Structure) (www.freepatent.com[13]). The optical constants such as thickness, refractive index, surface morphology, and transmission measured by Ellipsometer, Atomic force microscope and spectrophotometer.

Deposition of Titanium film in thermal evaporation meted

Deposition condition:

Material : Titanium (99.99 % pure)

Resistance: Tungsten filament

Substrate: Optical glass $70*70mm^2$

Oxygen gas not used.

Base pressure ($4*10^{-5}$ torr)

Power supply: For HT voltage=3.5KV, current=500mA for 5 minutes

For LT voltage=20v, current=170A

The deposition process of all films on the glass substrate explained above in CHAPTER 1.4..So the deposition of Ti film also same process as all films but high melting point that is 1750^0c.

- The cleaned substrate ($70x70mm^2$) is loaded on the substrate holder.
- Evaporation sources are filled with required amount of material to be evaporated.
- The base pressure of about 4*10^ -5 torr is attained.
- For evaporation of Ti given High current and Low voltage.
- While deposition is going set the Transmission up to 6%.
- After deposition check the characterization

4. CHARACTERIZATION BEFORE HEAT TREATMENT:

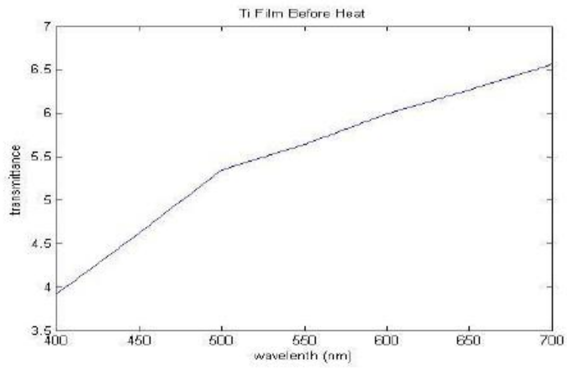
Spectro photometer Results:
Ellipso Meter results:
Atomic Force Microscope results:

Spectro photometer Results: **Table 1**

S.NO	Wavelength (nm)	Transmittance %
1	400	3.92
2	450	4.62
3	500	5.35
4	550	5.64
5	600	5.99
6	650	6.27
7	700	6.57

Graph:

Wavelength Vs Transmission

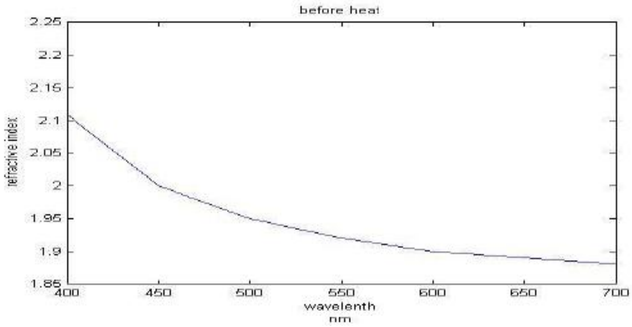


Graph 1

Ellipso Meter results:

S.no	Wavelength(nm)	Refractive Index
1	400	2.11
2	450	2.0
3	500	1.95
4	550	1.92
5	600	1.90
6	650	1.89
7	700	1.88

Graph: wavelength VS refractive index



Graph 2

Result of spectrophotometer, Ellipsometer:

It was observed from the above results that transmittance of the film increases and refractive index decreases with the increase in the wavelength (Practical guide of Hind High vacuum documents[5]).

Atomic Force Microscope results:

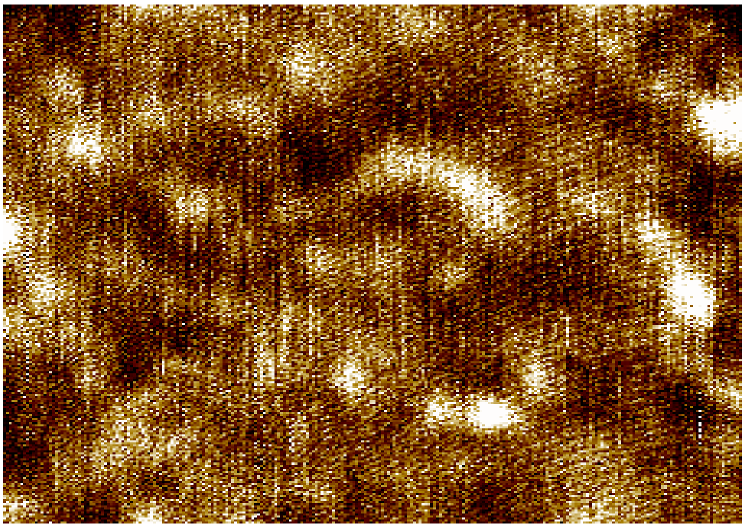


Fig 10

The structure of Ti film at room temperature of the film having n 1.7, t 30nm and T 6% at 550nm .

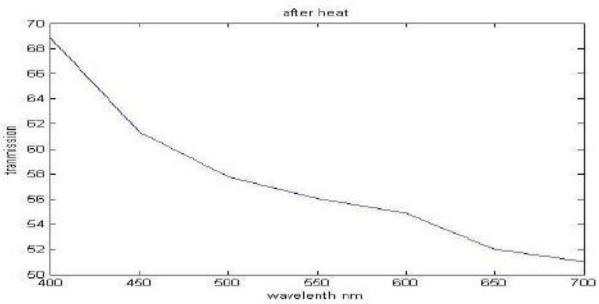
Characterization (after heat treatment)

Spectrophotometer Results:

Table 2

S.NO	Wavelength (nm)	Transmission %
1	400	68.92
2	450	61.35
3	500	57.59
4	550	56.04
5	600	54.86
6	650	52.01
7	700	51.01

Graph: Wavelength (nm) Vs Transmission%

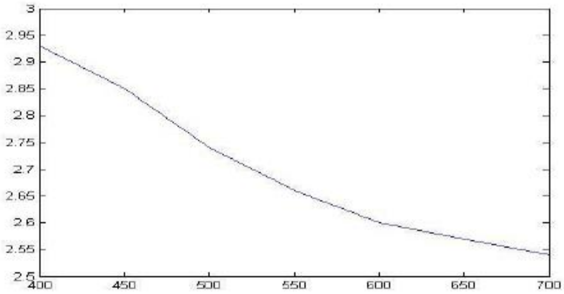


Graph 4

Ellipso Meter results:

S.no	Wavelength(nm)	Refractive Index
1	400	2.93
2	450	2.85
3	500	2.74
4	550	2.66
5	600	2.60
6	650	2.57
7	700	2.54

Graph:
Wavelength (nm) Vs Refractive index



Graph 5

Result of spectrophotometer, Ellipsometer:

It was observed after heat treat treatment Tio_2 film transmittance increased from (6% to 60%) at 550 wavelength, Due to change in film structure. Before heat treatment Ti film was hexagonal structure after heat Ti changes to TiO2 and structure transform into more stable rutile (porous) due to this rutile structure the film was not continues like some portion heavy thicker some portion totally transmittance (K.L. Chopra[6]).

When increases the wavelength, transmittance of film decreases due to high refractive index of film..While increasing the wavelength the energy of the waves decreased that low energy waves unable to pass throw the film so some of waves reflects from the TiO_2 film

Atomic Force Microscope results:

Tio_2 film after heat treatment the film structure transformed (hexagonal to rutile), T 60% at λ=550(nm) , refractive index is 2.6 and thickness is 60nm

Theory of humidity sensor:

The humidity detection would be depend significantly on the thickness of deposited film as the extent of abrasion of water molecules depends on it.

If film thickness increased the response time of film increasers for required thickness THERMAL EVAPORATION TECHNIQUE is better than CVD technique

The sensitivity of our sensors varies as a function of humidity due to the change in resistance.
The maximum sensitivity occurs approximately 70% RH

Adsorption and desorption of water molecules:

Since water is a polar molecule, the negative charged oxygen of the water molecule is Electro statically attracted to the positively charged cationic (Ti^{+4}) side of the metal oxide surface. If the charge density of the cationic side is low, then the water remains physically adsorbed at the surface by a weak Electro static field . when the cationic charge is high, as in the case of alkali salts, the electro static force high enough to form chemical bond between hydrogen and oxygen of a water molecule, which in turn may break bond between oxygen and one of the hydrogen atoms mostly the force is high enough to break the bond in the initially adsorbed water vapor layer. therefore the initial monolayer is generally chemisorbed. This chemisorbed layer can be thermally removed by increasing the ambient temperature (www.freepatent.com[14]). The irreversible reaction for the first layer can be given as

$M^+ + H_2O \text{--------}\rightarrow M - OH + H^+$

The subsequent water layers are physically adsorbed on the first chemisorbed layer. This physisorbed water layer is bound by weak electrostatic force (known as hydrogen bonding) on the underlying chemisorbed layer and can be reversibly removed by decreasing humidity. Therefore, this layer is mostly contributed for the humidity sensitive conduction of ceramic materials (Holland[7]). The chemisorbed water molecules exert an electrostatic field which not only attracts water molecules, but also weakens the oxygen to hydrogen bonds of the physisorbed water molecules. The weakening action of the surface oxygen to hydrogen bonds of the physisorbed water molecules, but also weakens the oxygen to hydrogen bonds of the physisorbed water molecules. The weakening action of the surface electrostatic fields promotes the dissociation of a physisorbed water molecule in the following manner:

$2H_2O \leftarrow\text{--}\rightarrow H_3O^+ + OH^-$

In pure water, the fraction of dissociated water molecules is approximately 1 $x10^{-8}$, but in the physisorbed layer of the water molecules this fraction is approximately estimated to be 0.01.

Experimental setup and results:

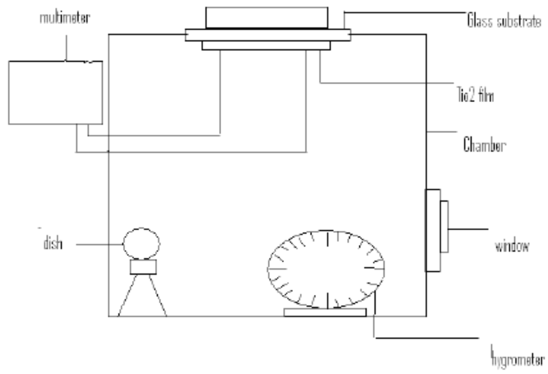


Fig 11 Humidity sensor

Measurements:

For measurements I made a thermo Cole chamber the coated glass 70*70mm glass fixed inside the humidity chamber the coated side of the film is inside the chamber.

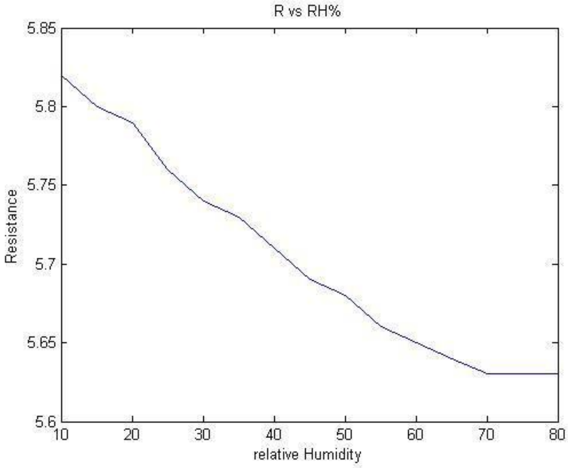
Two contacts made from the surface of film by crocodile clips. These contacts connected to the multimeter. One hygrometer placed inside the chamber to measure the humidity, temperature of the chamber

The least count of the hygrometer used here 1% RH K_2SO_4 is used as a humidifier the chamber and KOH is as dehumidifier. The humidifier/ dehumidifier is kept dish over the stand. The chamber is dehumidifier first up to 6% RH by using KOH The change in resistance of the film noted as relative humidity inside the chamber slowly increases 6 % to 70% (Surface and Coatings Technology[8]).The temperature inside the chamber was 32% the relative humidity indicates the hygrometer.

Result:

S.NO	Relative Humidity (RH%)	Resistance (k ohm)
1	10	5.85
2	15	5.80
3	20	5.76
4	25	5.74
5	30	5.73
6	35	5.71
7	40	5.69
8	45	5.68
9	50	5.66
10	55	5.64
11	60	5.63
12	65	5.62
13	70	5.62
14	75	5.62
15	80	5.62

Graph:
Relative Humidity Vs Resistance (k ohms)



Graph 6

Resistance in kilo ohms

While increasing the relative humidity decreasing the film resistance due to increasing the film conductance.

Applications:

- Food packaging, storage
- Flower packaging
- Vegetable packaging
- Measure humidity in houses, laboratories …etc

Used Instruments in experimental set up

- Hygrometer
- Multi meter

5. CONCLUSION:

Mainly we have concentrated the deposition of thin film coating for various applications. Almost above described coatings have done with the help of thermal evaporation. Thin films have wide applications in microelectronics, optics and nanotechnology .For humidity sensor, Tio_2 deposited on glass substrate . The Tio_2 film has high refractive index at visible and IR region and high transmission due to its rutile structure (porous structure).The TiO_2 film giving good adhesion with glass substrate .thickness of film is 60nm
The rutile structure of Tio_2 film is more sensitive to humidity at range (6% to 70%) RH.

REFERENCES:

1. Ronald R.Willey, A hand book of "Practical design and production of optical thin films".
2. H.A. Macleod, "Thin Film Optical Filters", 3rd Edition, Institute of Physics Publishing.
3. James D. Rancourt, optical thin films users hand book.
4. M. H. Hablanian.: High vacuum Technology: A Practical guide.
5. Practical guide of Hind High vacuum documents.
6. K.L. Chopra, a hand book of "Practical design and production of optical thin films".
7. Holland, "a hand book of optical thin film coatings".
8. Surface and Coatings Technology Volumes 120-121, November 1999, Pages 303-312.
9. Langmuir (2007), Highly Sensitive Optical Detection of Humidity on Polymer/Metal Nanoparticle Hybrid Films. *23,* 3473-3477,

WEB REFERENCE:

- www.freepatent.com