Chapter -3

Thin Film Deposition Techniques

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THIN FILM DEPOSITION TECHNIQUES

3.1. INTRODUCTION

The optical and structural properties of films mainly depend upon deposition technique. Two dimensional material of thickness ranging from angstroms to hundreds of micrometer, can be prepared by a hust of so called thin film as well as thick film techniques. Both science and technological, applications have been responsible for development of thin film technology [101-102]. Some important features of thin film science & technology are.

1. Low consumption in devices.
2. Higher packing density.
3. Nearness to a two dimensional structure as an aid to study material in general.
4. Preparation of innovative materials
5. Reliable electrical contracts.
6. Productive coating
7. Possibility of miniaturization.
8. In-situ junction and electrode preparation.

Approximately, for thickness > 1000A^o the bulk and film properties are same. Scientifically, it is convenient to call films from monomolecular layer (~5-10A^o) to 1000 A^o as thin films and beyond this it is thick film [103].

A thin film deposition process involves three steps

1. Creation of atomic/molecular/ionic species,
2. Transport of these species through a medium.
3. Condensation of the species on a substrate.

In the present work we have used vacuum deposition technique for the preparation of the sample.

3.2 VACUUM DEPOSITION TECHNIQUE

3.2.1 Kinetics

It is the important technique for thin film preparation. The evaporation of any material requires that the material should be heated to a sufficiently high temperature to produce the desire vapour pressure. The rate of free evaporation of vapour atoms from a clean surface of unit area in vacuum is given by the Langmuir-Dushman Kinetic theory equation:

$$Ne = 3.513x\ 10^{22}\ P_e/\ (MT)^{1/2}\ \text{molecules}\ cm^{-2}\ S^{-1} \qquad \cdots\cdots\cdots(3.1)$$

Where P_e is the equilibrium vapour pressure (in torr) of the evaporant under saturated vapour conditions at a temperature T and M is the molecular weight of the vapour species. The vapour atoms transverse the medium and are made to condense on a substrate surface to form thin film. The rate of condensation and deposition of the vapour atoms depends on the vapour-source substrate geometry and the condensation coefficient on the surface under given physical conditions.

The vapor atoms are scattered by collisions with residual gas atoms in the vacuum system. The scattering probability is $e^{(-d/\lambda)}$, where d is the source substrate distance and is the mean free path of the gas atoms. Also the gas

molecules impinge on the substrate surface at a rate given by equation 3.1 where of course the parameters T, M and P_e refer to the gas molecules at temperature T. It was found from experiments that vacuum of 10^{-5} torr to 10^{-7} torr is good enough for deposition of clean films except those readily oxidizable in which case relatively much better vacuum conditions are required.

3.2.2 The Essential Condition of Vacuum

Solid materials are heated up to high temperature to vaporize them thus these vapours are condensed onto a surface from a thin solid film. The vacuum evaporation is essential because.

(i) The material will heat at a lower temperature in vacuum.

(ii) The effect of oxides can be minimized formed on boiling surface boiling on the surface.

(iii) The number of impurities in the deposited material can be minimized large enough.

(iv) It is possible to mask between source and the substrate and obtain a sharp pattern on the substrate.

(v) The main advantage of the vacuum is that the adhesion of the film increase due to increase in (mean free path) and better film can be formed. The grain size of the atoms also increases and the film formed will again be a better film. When the vacuum is there then less number of atoms or ions are present and the successive time of the two collisions increases. Due to this there will be less number of collisions and the atoms and will have

more energy resulting loss of energy will be less. Finally the atom and ion will strike at the substrate with more kinetic energy (or velocity) so that the adhesion will better. So the adhesion can maximize.

3.2.3 Process of Heating in Vacuum Evaporation Technique

The evaporation of the material in a vacuum system requires a source to support the evaporant and to supply the heat of vaporization. The vacuum evaporation requires three factors that are

(i) Source

(ii) Evaporation (material to be evaporated)

(iii) Substrate (on which film is to be formed or deposited and it should be chemically washed and highly cleaned).

The simplest sources are resistance heated wires and metal foil of various size and shapes. Generally Tungsten (W), Molybdenum (Mo) and Tantalum (Ta) are used as a resistance heated wires and metal foil because they have high melting points and low vapour pressure.

The source can be designed in the Laboratory by bending sheet into the desire shape. Wetting of the metal foil surface by the molten evaporates desirable in the interest of good thermal contact, but molten metal also lower the electrical resistance of foil causing the temperature to drop. This problem is avoided with oxide coated foils.

The problem of finding non-reactive supports for materials evaporating above 1000°C can be over comes in these cases when vaporization

temperatures is near to the melting point of the evaporant. The materials such as M_0, V and Si, reach vaporization temperature before they melt and hence can be sublimated. This allows evaporation from wires or foils of the film materials by direct resistance heating without contact with any foreign martial. High purity, nickel and iron films have been prepared by this method.

Vaporization of the substance can also be done by electron bombardment instead of supplying energies by resistance of induction heating. A stream of electron is accelerated through field of 0.5 to 10 KeV and focused onto the evaporant surface. Most of the K.E of the electrons is converted into heat and temperature exceeding 3000° C many be obtained. It can be concentrated on the evaporation surface while other portions of the evaporation are maintained at lower temperature. Hence interaction between evaporation and support material are reduced.

3.2.4 Vacuum Set Up

Vacuum evaporation requires a system with a known vacuum and its residual gas analysis. A diffusion pump backed by a rotary pump system continues to be 10^{-6}-10^{-8} torr workhorse in the film technology largely because of its modest price, simplicity and high speed. By using special diffusion pump oil (e.g. poly phenyl ether), a cryogenic baffle, and all metal system, ultra high vacuum in the range 10^{-8} to 10^{-10} torr are easily obtained. The second most common system is based on sputter ion pumps backed by sorption pumps and assisted by a Ti sublimation pump, cryo-pump system using clocked cycle, He-temperature probes are the new and the clean, but more expensive, additions in the UHV field. It must be noted that each

vacuum system has its own character from the point of view of pumping characteristics, vacuum and residual gas composition. Further, each system may interact with a thin film condensation process in its own way [104].

Besides a vapour source, one requires numerous other accessories in the vacuum system. These include shutters, substrate heaters, a planetary system, (for uniform deposition over large areas) and monitors and or controllers for deposition rate and films thickness.

All the accessories must necessarily be made of materials compatible with UHV technology form the point of view of degassing and chemical reaction with the required vapors. The deposition rate is commonly monitored and controlled with the help of a quartz crystal oscillator, ion current in a nude ionization gauge and an appropriate mass spectrometer. In view of their important role in obtaining film of desired properties a detailed understanding of the deposition accessories is essential.

In our laboratory, for vacuum evaporation we have used vacuum coating unit (Fig. 3.1 & 3.2) for the preparation of the thin film. The description of this model in brief has been given as follows.

3.3 VACUUM COATING UNIT

Introduction

Vacuum coating unit can cover large number of laboratory applications like preparation of thin films for optical and electronic application, preparation of specimens for electron microscope etc. This basic unit consists of a cabinet containing a vacuum pumping unit together with the entire electrical

component necessary for the coating process. The vacuum coating machine consists of following main parts:

1. Vacuum system
2. Evaporation chamber
3. Heating arrangement
4. Feed through
5. An additional arrangement for ampoule evacuation.

The vacuum system consisted of a rotary pump and a diffusion pump. The rotary pump capable of attaining 10^{-3} torr vacuum is used as backing device for diffusion pump which ultimately creates a vacuum of the order of 10^{-5} torr. Diffusion pump can achieve the vacuum of 10^{-6} torr. Thin films were deposited in a vacuum of 10^{-5} torr.

Evaporation of the material in a high vacuum evaporation chamber requires a source in the form of boat or filament to support the material and to supply the heat for vaporization, the material to be evaporated and a substrate on which film is to be deposited. The source used was Molybdenum (Mo) boat because of it has high melting point and low vapour pressure.

Figure 3.1 Photograph of vacuum coating unit

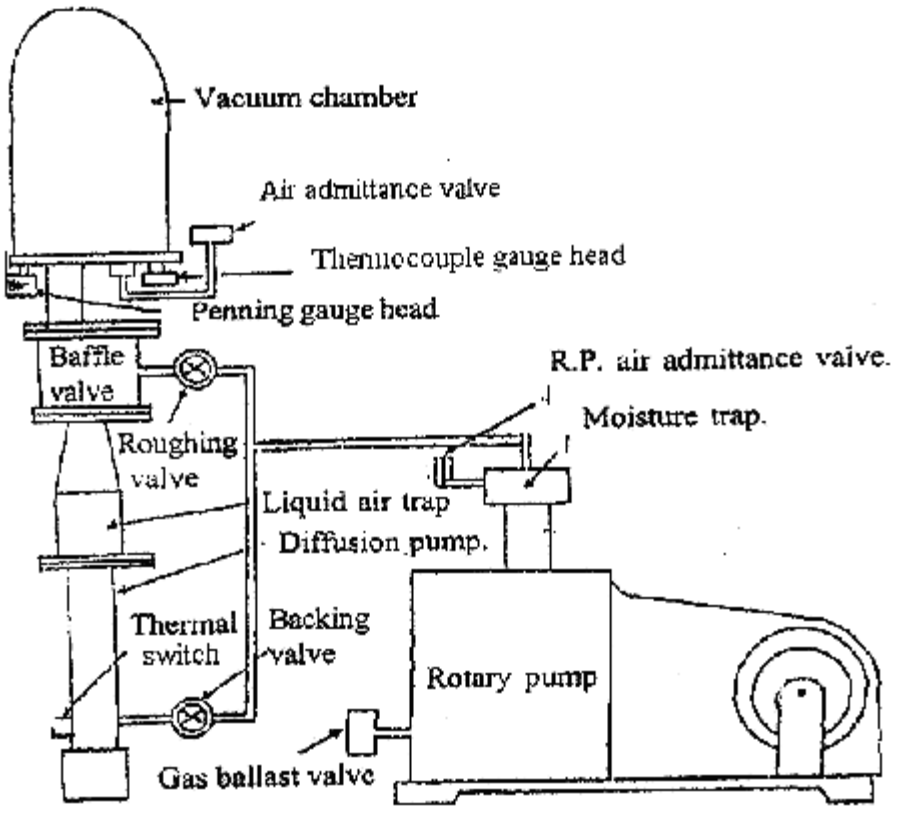


Figure 3.2 Schematic representation of vacuum coating unit

VACUUM CHAMBER

The vacuum chamber is fabricated from Pyrex brand glass. When the chamber is

A cooling water pipeline is attached to the outside of the chamber to prevent overheating, and to reduce the out gassing by circulating the water. A Pyrex brand glass beljar is also there for the coating unit.

PUMPPING SYSTEM

The chamber is evacuated by Model OD-114 oil diffusion pump and backed by a 200 liters per minute double stage gas ballast rotary pump V-belt driven from a 3/4" H.P. Motor with overload protection. The effective speed to the pumping 180 liters per second.

PRESSURE ACT

A model STA 6P3/STC 2P3- Priani / Thermocouple- Penning joint gauge fully established is provided. This gauge operates in conjunction with two Pirani /two thermocouple gauge heads, one mounted in the rotary pump pipeline and the other in the chamber. The penning gauge head is mounted to the camber. The Pirani / thermocouple gauge measures from 0.5 torr to 10^{-3} (one micron) and the penning gauge measures from 10^{-2} torr (10 microns to 10^{-6} torr) or (0.001 microns).

Pirani / Thermocouple gauge is used to measure roughing and backing pressure and penning gauge is used to measure five pressures in the chamber.

ACCESSORIES

(A) Diffusion Pump

Diffusion pump are a type of vacuum pump designed to achieve better vacuum pressures than possible by use of mechanical pumps alone. They use a high speed jet of fluid to direct residual gas molecule in the pump throat down into the bottom of the pump and bring out the exhaust through mechanical pump. The high speed jet is generated by boiling the fluid and directing the vapour through a multistage jet assembly. The out side of the diffusion pump is cooled using either air flow or a water line. As the vapour jet impacts the outer cooled shell of the diffusion pump the gas entrained in the jet flow coalesces, carrying the entrained pumped gases in to the base of the pump where the gas pressure is increased and pumped by secondary mechanical from the diffusion pump outlet.

(B) Rotary pump

The rotary pump is useful for deposition of materials uniformly on large plane surface substrates. A vacuum of the order of 10^{-3} Torr is obtained using rotary pump. This comprises of a rotating work holder which has a useful diameter of 6 . The work holder ring is supported by three equally spaced ball bearings one of which is spring loaded acting on the rim of the

work holder. The work holder is rotated by a variable speed electric motor situated on a plate form inside the coating unit cabinet. The pump is brought into the vacuum system through a reduction gear box through universal joints and shaft seal and communicated to the rim of the work holder by a friction gear and through an idler gear which is filled with two rings for the vibration free operations. The speed of the rotary drive motor is controlled by a solid state speed control fitted on the front left hand side pillor.

(C) Off sector Ion bombardment

This is used in conjunction with the rotary drive. This high tension discharge cleaning system consisting of radiant super pure aluminum electrode bar. The bar is shielded to avoid electron contamination of the substrate during discharge cleaning.

(D) Source shutter plate

This source shutter plate is designed to cover any one of the off sector filament holders meant for sequential evaporation when a rotary drive is used. The shutter plate is attached to standard source shutter shaft when a rotary drive is used.

(E) Off sector filament holder

This filament holder is used in conjunction with rotary drive. They are designed to distribute uniform evaporation on a rotating plane substrate held in the rotary work holder ring.

MULTIFILAMENT TURRET

The multi element turret is designed to evaporate four different materials vertically below the current of the work holder ring without breaking the vacuum. There is no provision to evaporate from off sector to be used with the rotary drive, so this gadget only is to be used with spherical work holder for multi layer depositions.

This thermal evaporation system consists of four positions vapour source turret constructed in copper permitting current loading up to 100 amps. The low tension earth brush is in permanent contact with the rim of the turret current low tension earth plate and low tension line electrode brush will make the contact when ever the evaporation source comes to the firing position (i.e., to center). The turret, which is supported on a circular plate, positioned 3", above the base plate from base to filament is rotated by external hand wheel. The movement is transmitted in to the vacuum system via1/4". Wilson shaft seal and a chain drive. The evaporation is carried out from the vapour source position vertically below the centers of the work holder ring each source can be adjusted to evaporation position by observing through the chamber window and that particular number of the source can be identified at the hand wheel indicator.

RADIANT HEATER

The radiant heater is fixed inside the chamber on top of the work holder ring. This can be easily installed and removed through the plug in type leads. This is capable of heating the substrate up to a temperature range of 250^{o} to 275^{o} about 30 minutes. The heater element in Nichrome and has a power rating

of about 500 watts 120V to 140V, one of the revolutions of the Variac control is used and the circuit is fused at 5 amps. to prevent over loading of the heater. Electrical connection is made via two loads fitted through the base plate.

Temperature measurement is made using a chromel-Alumel thermocouple in conjunction with 500°C meter mounted on the meter panel. The thermocouple leads are brought out of the vacuum system via a multi-pin lead through the base plate.

ELECTRON GUN

The electron gun is a vapour deposition source designed to produce thin film in higher vacuum. The gun can achieve temperatures in excess of 3000° C. This is readily adequate to produce thin metallic and non-metallic film of the refractory metals thin metallic and non-metallic film of the refractory metals, such as tungsten, tantalum and molybdenum. The material holder is water-cooled copper.

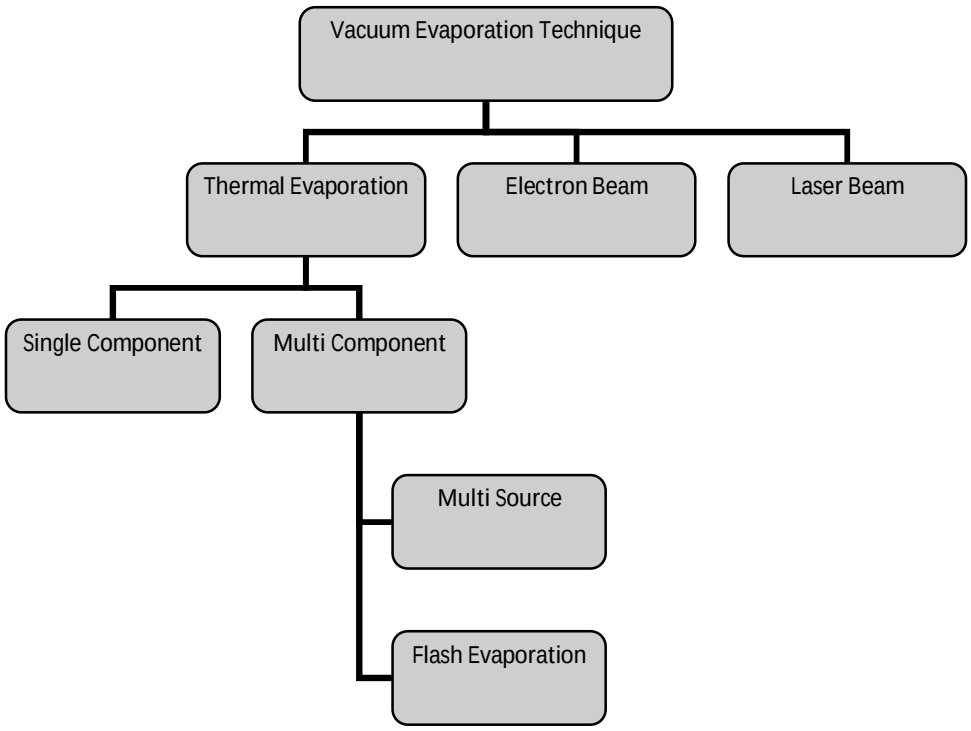
The gun consists of three principal parts, a water-cooled sample holder (anode), a filament (cathode) and a shield. In operation the filament is resistively heated by a filament power supply to the point where it admits electrons. One end of the filaments is connected to the shield. This prevents electron from being accelerated by striking the shield. The sample holder is kept at several K.V. positions with respect to the filament and shield by high voltage supply. This causes the electrons, which have been emitted by the filament to be accelerated to wards and strike the sample in the sample holder. On striking they give up energy that they gained during acceleration, heating the sample to the point where it evaporates. The shield prevents the

evaporated material from leaving the gun in any direction other than through the part made in the top shield. A power supply consisting of H.T and L.T. will meters and control will be supplementary with the gun.

With the help of the above coating unit we can achieve the pressure of about of the order of 10^{-6} torr.

ELECTRICITY SUPPLY

230V A.C Single phase 50 Hz amps and maximum power consumption is bout 3KVA. The vacuum evaporation technique can be classified as follows.



3.4 REACTIVE EVAPORATION

This technique is used to deposit the metal and their oxide films. In deposition of metal films, the background temperature is kept as low as possible because the interactions of residual gases with evaporant effect the film properties. However, in reactive evaporation, higher oxygen pressure is maintained to produce fully oxide metal films. This technique is applicable in those cases metal oxide cannot be evaporated directly because of complete or partial decomposition.

The reactive evaporation of metals or metals oxides on to substrate at moderate temperatures, produce amorphous or fully crystalline films whose stoicheometery is largely determined by the impingement ratio of the constituents. However, because of the differences in the condensation ratio, film composition is not the same as impingement ratio. In metal oxides, which have been reactively evaporated, the deposition rates are small to ensure a high impingement ratio to increase the oxygen pressure, the existing studies pertain mostly to oxide, and reactive evaporation is applicable to other classes of compound also.

3.5 SINGLE COMPONENT EVAPORATION

The single component can easily evaporate with the help of resistance-heated wires or boat and finally the film is deposited on a substrate.

3.6 MULTI SOURCE EVAPORATION

In this case multi components alloys or compounds are thermally evaporated. The composition may evaporate may evaporate at different at

different rate because of their different vapour pressure due to their different tendencies to react with support material.

A satisfactory method to prepare alloys and compounds with precisely controlled composition is to evaporate each component from a separate source. The growth of the film can be controlled (thickness and growth rate) with the help of thickness monitor and growth rate monitor.

3.7 FLASH EVAPORATION

Flash Evaporation is another technique for the deposition of the film whose constituent has different vapour pressure. The film composition is accomplished by evaporating small quantity of the constituents in the desire ratio. Only one filament is used at a temp. (Sufficiently high) to evaporate the material.

In the above case the evaporation of material is only possible in the powder form and not in the wire form. Flash evaporation is performed in vacuum of the order of 10^{-5} torr. This technique has been used to prepare single-phase pseudo binary compounds of different groups and multi components alloys.

3.8 LASER EVAPORATION

The high intensity of the laser can be used to heat and vaporize material by keeping the laser source outside the vacuum system and focusing the beam on to the surface of a material to be evaporated. But the disadvantage is, since the layer penetration depth is small (~ 100 A°) evaporation takes place at the surface only. Non-Q-spoiled glass neodymium laser is used to deliver 80 to 150 J of energy per burst with ft duration of 2 to 4 m Sec. To evaporate the materials all film deposition technique has their own characteristics. Thin

film technology is most widely used for discrete devices and vacuum deposition is the most sought for method of preparation of thin films of polymers [105-108].