3. INTRODUCTION

Thin films can be prepared from a variety of materials such as metals, semiconductors, insulators or dielectric etc, and for this purpose various preparative techniques have been developed [1-2]. Newer methods are also being evolved to improve the quality of the deposits with maximum reproducible properties.

3.1. PHYSICAL VAPOR DEPOSITION

The most important characteristic feature of physical vapor deposition technique is that the transport of vapors from the source to the substrate takes place by physical means. This is achieved by carrying out the deposition essentially in a vacuum of such magnitude that the mean free path of the ambient gas molecules is greater than the dimensions of the deposition chamber and the source-to-substrate distance. Under such low-pressure ambient conditions, the transport of the material from the source to the substrate occurs by molecular beams. The vapor species of a solid material may be created either by thermal evaporation or by sputtering process.

The three fundamental steps include

(i) Vapor phase generation by coating material

(ii) The transfer of the vapor phase from source to substrate
Deposition and film grouter on the subs tract

The selection criteria for determining the best method of physical vapor deposition depended on several factors

- Type of the material to be deposited
- Rate of deposition
- Limitation imported by the substrate
- Equipment requirements and their availability
- Cost
- Ecological Conditions
- Adhesion of the deposition to the substrate
- Throwing power

3.1.1. VACUUM EVAPORATION

Material can be heated in a vacuum and evaporated, to deposit on a substrate [3]. This requires a vacuum chamber and a pulping system, sample holder, crucible for the evaporate, and a shutter. The vacuum chamber is pumped to $10^{-6} - 10^{-7}$ Torr ($10^4 - 10^5$ pa).

This pressure gives a mean free path of $\sim 10$ cm from the evaporated molecules. The source is heated using a tungsten filament or electron beam
Evaporation rate is related to the material vapor pressure. At a given temperature there will be a pressure of material vapor above the source. Low melting temperatures materials are easier to evaporate.

Evaporated material originates at a purists source, and does not scatter match is transit to the substrate, so substrate coverage is generally line-of-sight.

3.1.2. THERMAL EVAPORATION

These techniques were adopted for the deposition of metals, alloys and also many compounds such as oxides, sulphides and halides [4-6]. Thermal evaporation uses the atomics cloud formed by the evaporation of the coating metal in a vacuum environment to coat all the surfaces in the line of sight between the substrate and the target. It is often used in producing thin films of 5μm. There coating however is fragile and not good for wear applications. The thermal evaporation process can also coat a very thick, 1mm a layer of heat-resistant materials.

3.1.3. ELECTRON BEAM EVAPORATION

It is one form of physical vapor deposition is which a target anode is bombarded with an electron beam gives off by tungsten filament under high vacuum [7]. The electron beam causes atoms from the target to transform into gaseous phase. These atoms then precipitate into solid form coating everything in the vacuum chamber with this layer of the anode material. EBPVD yields a
high deposition rate from deposition rate from 0.1μm per minute
is at relatively low substrate temperatures, with very high material
utilization efficiency.

In EBPVD systems, the deposition chamber is evacuated to
a pressure of $10^{-4}$ torr. The material to be evaporated is in the
form of ingots. The generated electron beam is accelerated to a
high kinetic energy and focused towards the ingots. When the
accelerating voltage is between 20kv-25kv and the beam current
is a few amperes, 85% of the kinetic energy of the electrons is
converted into thermal energy as the beam bombards the surface
of the ingot. The surface temperature of the ingot increases
resulting in the excitation of x-rays and secondary emission, the
liquid ingot material evaporates under vacuum. The evaporation
rate may be of the order of 10-2 g/cm² sec.

3.1.4. SPUTTERING

Sputtering is another common deposition technique, which
overcomes some of evaporation. Sputtering requires a vacuum
chamber; a sample holder, a sputtering target of the material to
be deposited, a gas delivery and pressure control systems and a
DC or RF power supply.

The chamber is evacuated to 10-6 10- 11 torr (10-4 10-9
pa). The power supply is used to ignite plasma with the chamber
grounded and the target material negative.
Positive ions from the plasma are accelerated toward the target and strike it with sufficient energy to create a collection cascade and eject target at once with much lower energies.

Higher energy leads to dense films. Distributed target is suitable for mass production and combined with scattering at high-pressure leads to reasonable step coverage.

Diode sputtering simply uses two electrodes magnetic sputtering uses magnets behind the targets to enhance the plasma density, rate, and electron flux to the substrate. Dc sputtering is good for conductors. RF is necessary for the insulating targets or some reactive process. Material properties can be controlled by pressure, power, and temperature.

In reactive sputtering compounds are often sputtered using an elemental target and a reactive gas. Particularly with metal oxides and provide control over stoichiometry.

The reactive gas will react with the target surface [8-10], often creating an insulation layer and reducing the sputtering rate. Usually for higher rate the system kept in metal mode just on the range of poisoning the target. Reactive sputtering processes are often characterized by the systems impedance changes as the gas mixture is changed.

Reactive evaporation has the coverage and control advantages of regular sputtering. Reactive evaporation is
occasionally used, but the substrate usually needs to be heated to get any reaction.

3.1.5. CATHODIC ARC DEPOSITION

Cathodic arc deposition is a technique in which an electric arc is used to vaporize material from a cathode target. The vaporized material then condenses on a substrate, forming a thin film[11-13]. The technique can be used to deposit a metallic, ceramic and composite films. This is also quite extensively particularly for carbon-ion deposition to create diamond like carbon films. Because the ions are blasted from the surface ballistic ally it is not common for not only single atoms, but larger cheaters of atoms to be ejected. This kind of system requires a filter to remove cluster from the beam before deposition.

Plasma beams from catholic arc source contains some large clusters of molecules (so called macro particle), thus preVent is from some kind of use without filtering. There exist many designs of macro-particle filters.

3.1.6. PULSED LASER DEPOSITION

Pulsed laser deposition is a their film deposition technique where a high power pulsed laser beam is to cussed inside a vacuum chamber to strike a target of the desired composition. Material is ten vaporized from the target and deposited as at their film an substrate [14], such as silicon wiser facing the target. Thus process can occur in ultra high vacuum of in the presence of
a background gas, such as oxygen, which is commonly sued when depositing oxides to fully oxygenate the deposited films.

While the basic-setup is simple relative to many other deposition techniques, the physical phenomena of laser-target interaction and film growth are quite complex. When the target absorbs the laser pulse, energy is first converted to electronic excitation and then into thermal, chemical and mechanical energy resulting in exasperation, ablation, plasma formation and even exfoliation. The ejected species expand into the surrounding vacuum in the form of a plume containing many energetic spicier including atoms, molecules, electrons, ions, clientless, particular and molder globules, before depositing on the typically.

3.2. CHEMICAL METHODS
3.2.1. ELECTRO DEPOSITION

Electroplating is an electrochemical process by which metal is deposited on a substrate by passing a current through the bath. The bath consisted of an anode, which is the source of the material to be deposited, the electrochemical which is the medium through which metal ions are exchanged and transferred to the substrate to be coated, the other metal is cathode which is the negatively charged electrode where the material is to be deposited is the substrate.
When the current is applied, positive metal ions from the solution are attached to the negatively charged cathode and deposit on the cathode. As replenishment for these deposited ions, the metal from the anode is dissolved and goes into the solution and balances the ionic potential.

Plating governed by Faraday's law that state

The weight of a substance formed at an electrode is proportional to the amount of current passed through the cell.

The weight of different substances produced at an electrode by the same amount of current is proportional to their equivalent weights.

There are many possible combinations of the bath constituents, which result in numerous formulations of bath compositions for each type of metals [15]. Baranski and Fawcett [16] have used to deposit thin films of semiconducting metal chalcogenides such as cadmium sulphide and lead sulphide on various substrates. Milazzo [17 and Brenner [18] had given reView for this technique.

3.2.2. ELECTROLESS DEPOSITION

The uniqueness of the process is that certain metals immersed in the solution and proceeds in a controlled manner on the substrate's surface catalogue the reduction. The deposit itself continues to catalogue the reduction reaction so that the
deposition process becomes self-sustaining or auto catalytic. These features permit the depositions of relatively thick deposits. Thus the process is differentiated from other types of chemical reduction by simple immersion or displacement reactions in which deposition ceases when equilibrium between the coating and the solution is established.

Homogenous reduction where deposition occurs over all surfaces is contact with the solution.

To prevent spontaneous reduction, other chemicals are present; these are generally organic complexing agents and buffering agents. The cost of the complexing and reducing agents used in electro less plating solutions make them non-competitive with electroplating procuress. The applications with electro less plating are usually based on one or more of the following advantages over electroplating.

Deposits are very uniform without excessive build-up-on corners or projections or insufficient thickness in resented areas. The uniformities are limited only by the ability of the solution to contact the surface.

Deposits are usually less porous and more corrosion resistant than electroplated deposits.

Electrical contacts are not required.
The deposits have unique chemical, Mechanical, Physical and magnetic properties.

By this method not only inactive metals but also non-conductors can be deposited with the help of suitable sensitizing and activating solution treatments [19]. The metal deposition can be carried out both in acidic and alkaline solutions.

This process is originally developed by Brenner and Riddell [20] for metals like nickel, platinum, but Goswami [21] observed metal such as brass, copper, lead could be coated by electro less process

3.2.3. CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials. CVD is used in a multitude of semiconductor wafer fabrication process including the production of amorphous and polycrystalline thin films.

During the process of CVD, the reactant not only react with the substrate material at the wafer surface but also in gas phase reactors atmosphere. Reaction that taken place at the subtract surface are known as reaction and are selectively occurring on the heated surface of the wafer where they heated good-quality films.
Reaction that takes place in the gas phase is known as homogeneous reaction. Homogeneous reaction from gas phase aggregate of the depositing material which adhere to the surface poorly and at the same time they form low-security films with lots of defects. Heterogeneous reaction are more desirable than homogeneous reaction during CVD.

There are many ways of desorbing or climaxing a CVD reactor, is said to be a hot-wall. If it uses a healing system that wets of the reactor or heating systems that minimize the heating up of the reaction walls is much the same way as they are deposited on wafers because this reactor requires frequent wall cleaning.

Another way of climaxing CVD reactor is by biasing it in the range of their operating pressure to atmosphere pressure. CVD reactors operate at atmosphere pressure. There for simpler in design. Low-pressure CVD reactors operate the medium vacuum and it require higher temperature thus APCVD. Plasma enhanced CVD reactors also operate under lower pressure, but do not depend completely on thermal energy to accelerate the reaction process.

Materials such as Oxides [22-23], sulphides [24] are prepared by chemical vapor methods. Diamond and Diamond like carbon films [25] are mostly prepared by this method.
3.2.4. LOW PRESSURE CHEMICAL VAPOR DEPOSITION

One of the significant developments in semiconductor device processing was the introduction of CVD reactors that operate at lower atmospheric pressure.

Depending on how much below atmospheric pressure the CVD reactor operates, three different process regimes have been distinguished. From 100 torr to 1 torr we speak of reduced pressure CVD (LPCVD), while LPCVD is commonly practiced in the range from 1 to 10 torr. To compensate for low pressure of operation relative to 760 torr is APCVD reactor; the input reactant gas cementation must be corresponding enriched to maintain comparable deposition rates. Low gas pressure enhances the mass flux of gaseous reactants and the products through the boundary layer. In a LPCVD reactor the gas flow velocity is generally a factor of 10-100 times higher, the gas density a factor of 1000 lower and the viscosity unchanged relative to APCVD.

Efficient film growth is limited by non-transport through the boundary layer of the following pores to overcome this barrier wafers are laid parallel to the gas stream. In LPVCD reactors, gas molecules have a layer means free path and greatly enhanced diffusivity. Gas will readily impinge on the wafers and deposition is no-longer mass - transfer limited but rather reaction rate controlled. This means that wafer can be stacked close together and parallel to each other.
One significant difference between atmospheric and LPVCD systems concerns the nature of deposition on reactor walls. Dense, adherent deposits accumulate on the hot walls of LPVCD reactor, whereas thinner, less adherent films form on the cooler walls of atmospheric reactors.

3.2.5. METAL ORGANIC CHEMICAL VAPOR DEPOSITION

MOCVD assumed additional importance is the deposition of assorted dielectrics and metals as well, other CVD process variants that are differentiated physically on the basis of pressure, on use of plasmas or photons. MOCVD is distinguished by the chemical nature of the precursor gases. The great advantage of metal organics is their generally high volatility at low temperatures. Since all constituents are in the vapor phase, precise electronic control of gas flow rates and partial pressure is possible without dealing with troublesome liquid or solid sources in the reactor. This combined with pyrolysis reactions, which for efficient and reactively insensitive to temperature, allows for efficient and reproducible deposition. Carbon contamination of the film usually carried out at low pressure, and sometimes with plasma assist.

Most CVD processes can be conveniently sub-divided into two categories. Thermal CVD processes employ heat energy to activate the required gas and gas-solid phase CVD reaction. In contrast, the plasma-enhanced CVD processes derive benefit
from plasma activation of the involved chemical species. Even with similar input gases used to deposit the same nominal materials, film produced by the same nominal materials, film produced by thermal and plasma CVD processes can widely differ with respect to film structure, composition and properties. It is an inexpensive thin film preparation method that employs metal organic precursors in a novel way [26-27]. Instead of being injected into a reactor as a gas, the precursors are directly to the substrate. Then a high temperature treatment decomposes the compound leaving the desired thin film.

The great variety of materials deposited by thermal CVD method has inspired the design and construction of an equally large number of processes and system.

3.2.6. ATMOSPHERIC PRESSURE CHEMICAL VAPOR DEPOSITION

There is a continual imperative to reduce semiconductor-processing temperature, the growth of high quality epitaxial thin film is often achieved by high temperature atmospheric pressure CVD. The reactors employed can be of two types namely hot wall and cold wall types. High temperature APCVD systems are also extensively employed in the deposition of hot metallurgical coatings [28,29]. One of the important advantage of CVD method is the ability to batch coat large number of small tools at one time since hard coatings are deposited on varied subtracts, such as carbides, high-speed steel tools, ball bearing steels, a wide
range of temperature is required, necessitating different deposition techniques and conditions deposition at temperatures as low as 300 degree Celsius is possible, but this requires operation is a plasma discharge.

3.2.7. PLASMA ASSISTED CHEMICAL VAPOUR DEPOSITION

Plasma assister chemical vapor deposition involves farming solid deposits by initiating chemical reaction in a gaseous discharge. The discharge can be exited by using RF, microwave, or photonic excitation. It produces a wide verity of chemical species ionized and excited states free radicals as well as ions and electrons. The nature, type, concentration and energy of these species determine the growth and properties of the films.

The important parameters controlling film growth by PACVD are as following,

Reactant partial pressure and flow rate

RF power

Substrate temperature and temperature bias

The above variables affect process parameters such as deposition rate on the one hand, and plasma parameters such as electron energy, and distribution function on the other. The partial pressure of the reactant gas together with RF power determines the rate of dissociation of the reactive gas and hence the dissociation rate. These same process variables also determine
the energy, so pressure and RF power also control the substrate bombardment. The substrate bombardment of the growing film and the deposition rate both are therefore dependent on the same set of process and plasma parameters makes it difficult to obtain high deposition rates by plasma assisted CVD processes.

3.2.8. PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

Plasma enhanced chemical vapor deposition is a process mainly to deposit thin films from a gas state on a solid state on some substrate. These are some chemicals reactions involved in the process, which occur after creation of plasma in the reacting gases [30,31]. The plasma is generally created by RF frequency or DC discharge between two electrode where is between place is filled with the reacting gases.

Plasma in any gas in which a significant percentage of the atoms or molecules are ionized. Fractional ionization in plasmas used for deposition and related materials processing varies from about 10^-4 is typical capacitance discharge to as high as 5-10% is high-density inductive plasmas. Plasmas with low fractional ionization are of great interest for materials processing because electrons are so light compared to atoms and molecules that energy exchange between the electrons and natural gas is very inefficient. Therefore, the electrons can be maintained at very high equivalent temperatures. These energetic electrons can induce many processes that would otherwise be very improbable.
at low temperatures, such as dissociation of precursor molecules and the creation of large quantities of free radicals.

A second benefit of deposition within a discharge arises from the fact that electrons are more mobile than ions. As a consequence, the plasma is more positive than any object it is in contact with. The voltage between the plasma and the object in contact is normally dropped across a thin sheath region. Ionized atoms are molecules that diffuse to the edge of the sheath region feel an electrostatic force and are accelerated towards the neighboring surface. Thus all surface exposed to a plasma receive energetic ion bombardment. The potential across the sheath surrounding an electrically isolated object is typically only 10-20V, but much higher sheath potentials are achievable by adjustments in reactor geometry and configurations. Thus films can lead to increase in density of the films and help remove contaminants, improving the films electrical and mechanical properties.

3.3. SOL–GEL METHOD

The Sol-gel process is a wet-chemical technique widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials of a metal oxide starting from a chemical solution. Sol-gel is a colloidal suspension that can be gelled to from a solid [32-39]. The resulting porous gel is then chemically purified and
fired at high purity oxide materials. The Sol-gel can be modified with a number depends to produce unique properties in the resultant glass unattainable by other means. It can be used in ceramic manufacturing process, as an investment casting material, or as a means of producing very thin metal oxides for various purposes, including a form superior to Teflon. Sol-gel derived materials have diverse application in optics, electronics, energy, space, sensors and separation technology.

The Sol-gel process involves the transaction of a system from a liquid into a solid phase. The Sol-gel process allows the fabrication of materials with a large vanity of properties.

The Sol-gel is made of solid particles of a diameter of few hundred nm, usually inorganic metal salts, suspended in a liquid phase. In a typical Sol-gel process, the precursor subjected to a series of hydrolysis and polymerizing reaction to form colloidal suspension. These particles condense in a new phase.

3.4. MOLECULAR BEAM EPITAXY

The most important aspect of MBE is the slow deposition rate (0.001 to 0.3 μm per minute), which allows the films to grow epitaxially. However, the slow deposition rate require proportionally better vacuum in order to achieve the same impurity level as other deposition techniques [40-42]. The terms beam simply means that exasperated atoms do not interact with
each other or any other vacuum chamber gases until they reach the wafer, due to long mean free paths of the beams.

During operation, RHEED is often used for monitoring the growth of the crystal layers. A computer control shelters in front of each furnace, allowing precise control of the thickness of each layer, down to a single layer of turns. In systems where the substrate needs to be cooled, the ultra-highs vacuum environment within the growth chamber is maintained by a systems of cry pumps, and cry panels, chilled using liquid or cold nitrogen gas to a temperature close to 77 Kelvin. In other systems, the wafers on which can be heated to several hundred degrees Celsius during operation.

Molecular beam epitaxy is also used for the deposition of same types of organic semi conductor. In this case, molecules, rather than atoms, are evaporated onto the wafer.

3.5. SPRAY PYROLYSIS TECHNIQUE

Chamberlin et al [43-47], Bube et al [48-54] at Stanford University had developed the spray pyrolysis technique. A review on this technique had been published by Chopra et al [58].

A large number of metallic salt solutions when sprayed onto a hot substrate decompose to yield sulphide films. It was used as early as 1910 to obtain transparent oxide films. In 1960’s Chamberlin et al extended the technique to produce sulphide and selenide films. The technique involves a thermally stimulated
reaction between clusters of liquid or vapor atoms of different chemical species. The spray pyrolysis technique involves different stages like spraying a solution, usually aqueous, containing soluble salts of the constituent atoms of the desired compound onto a substrate maintained at elevated temperatures. The sprayed droplet on reaching the hot substrate surface undergoes pyrolytic decomposition and forms a single crystalline or a polycrystalline film. The other volatile by products escape as a vapor during the thermal decomposition. The substrate provides the thermal energy for the thermal decomposition and subsequent recombination of the constituent species followed by sintering and recrystallization of the clusters of crystallites giving rise to a coherent film.

The chemicals used for spray pyrolysis have to satisfy the following condition. On thermal decomposition the chemicals in solution form must provide the species/complexes that will undergo a thermally activated chemical reaction to yield the desired thin film material and the remainder of the constituents of the chemicals, including the carrier liquid should be volatile at the spray temperature. For a given thin film materials, the above conditions can be met by a number of combinations of chemicals. However, different deposition parameters are required to obtain comparable quality films.
3.5.1. GROWTH KINETICS

When both the size and momentum of the spray droplets are uniform, optically good quality and smooth films are obtained. Limpkin [55] had studied the aerodynamics of the atomization and droplet impact processes and has correlated the dynamic features of the spray process with the kinetics of film growth and surface topography. The disk geometry depends on the momentum and volume of the droplet, the substrate temperature and the balance of the dynamical surface energy and thermal process [56-57].

The deposition processes a resultant of the following steps i) Spraying of a drop into a disk, ii) Pyrolytic reaction between the decomposed reactants iii) evaporation of the solvent, and iv) repetition of the preceding processes with succeeding droplets. Consequently the film generally contains disks interspread into each other. The lateral mobility of the droplets and coalescence and sintering kinetics of the super imposed disk crystallite clusters determine the growth kinetics and micro structural features of the spray deposited films. Thus spray deposited films are coherent and pinhole free even at very low (1000A) thickness, provided the substrate temperature is high enough to cause complete pyrolytic reactions and the temperature profile during the deposition process.

The spray nozzle effects the atomization of the chemical solution into a spray of fine droplets. The carrier gas and the
solution are fed into the spray nozzle at pre determined constant pressure. The temperature of the substrate is maintained by the coil, which is connected to the power supply. Scanning both the spray head and the substrate, by mechanical arrangements, attains entire substrate coverage. The size distributions of the droplets is determined by the factors such as spray rate, spray nozzle and the carrier gas.

3.5.2. SULPHIDES DEPOSITION

An aqueous metal salt solution is sprayed onto a hot substrate to obtain the corresponding metal sulphide films. Generally lead acetate, lead nitrate, lead chloride and thiourea have been used.

3.5.3. FEATURES OF THE SPRAY PYROLYSIS PROCESS

3.5.4. GROWTH RATE

The chemical nature, temperature of the substrate, and concentration of the spray solution, its additives, and the spray parameters largely determine the growth rate. The growth rates can be as large as 100 \( \text{A min}^{-1} \) for oxide films and 50 \( \text{A}^0 \text{min}^{-1} \) for sulphide films.

3.5.5. SUBSTRATE EFFECTS

Generally, at lower substrate temperature foggy and diffusely scattering films are obtained. High substrate temperature yields thinner, continuous, hard and spectrally scattering films. Moreover, at higher temperatures, re-
evaporation of anionic species may occur, leading to metal-rich deposits. In general the spray pyrolysis process affects the substrate surface. When it is not desirable for the substrate to take part in the pyrolytic reactions, neutral substrates such as glass, quartz, ceramics, mica, plastics substrates are employed. Metallic substrate [58] is not found to be suitable for this process.

3.5.6. PROPERTIES OF SPRAY DEPOSITED FILMS

Films prepared by spray pyrolysis are strongly adherent, mechanically hard, pinhole-free and stable with time and temperature. The roughness of the film is mainly depends on the substrate temperature and spray conditions. At annealing temperatures above the spray temperature, of under some reactive environments, recrystallization increases the grain size and may produce some preferential orientation effect [59].

REFERENCES:


43. R. R. Chamberlin, WPAFB contract NO AF 331657-7919 (1962).


