Thin Film Deposition Technology

1. Objective and Scope of This Section:

The aim of this section is to provide a concise reference and description of the processes, methods, and equipment for depositing technologically important materials. Emphasis is placed on the most recently developed processes and techniques of film deposition for applications in high technology, in particular, advanced microelectronic device fabrication that requires the most sophisticated and demanding approaches.

2. Importance of Deposition Technology in Modern Fabrication Processes:

Thin Film Deposition technology can well be regarded as the major key to the creation of devices such as computers, since microelectronic solid-state devices are all based on material structures created by the deposition techniques. Excellent stability and accuracy together with a level of reliability (which is not economically feasible with other technologies) of the electronic components and devices is the hallmark of thin film technology.

Electronic engineers have continuously demanded films of improved quality and sophistication for solid-state devices, requiring a rapid evolution of deposition technology.

Equipment manufacturers have made successful efforts to meet the requirements for improved and more economical deposition systems and for in situ process monitors and controls for measuring film parameters.

The improved understanding of the physics and chemistry of films, surfaces, interfaces, and microstructures made possible by the remarkable advances in analytical instrumentation during the past twenty years. A better fundamental understanding of materials leads to expanded applications and new designs of devices that incorporate these materials.

A good example of the crucial importance of deposition technology is the fabrication of semiconductor devices, an industry that is totally dependent on the formation of thin solid films of a variety of materials by deposition from the gas, vapor, liquid, or solid phase.

3. Classification of Thin Films Deposition Technologies:

A solid material is said to be in thin film form when it is grown as a thin layer on a solid substrate by controlled condensation of the individual atomic, molecular, or ionic species either by physical process or ultra-chemical reactions. There are many dozens of deposition techniques for material formation. Since, the concern here is with thin-film deposition methods for forming layers in the thickness range of a few nanometers to about ten micrometers, the task of classifying the techniques is made simpler by limiting the number of techniques to be considered.

Basically, thin-film deposition techniques are either purely physical, such as evaporative methods, or purely chemical, such as gas- and liquid-phase chemical processes. A considerable number of processes that are based on glow discharges and reactive sputtering combine both physical and chemical reactions; these overlapping processes can be categorized as physical-chemical methods.

The number of thin film materials, their deposition processing and fabrication techniques are used to produce the devices. It is possible to classify these techniques in two ways.

* Physical Vapor Deposition (PVD)
* Chemical Vapor Deposition (CVD)

Physical method covers the deposition techniques which depend on the evaporation or discharge of the material from a source, i.e. evaporation or sputtering, whereas chemical methods depend on physical properties and solid films are formed on the substrate by chemical reaction of vapor phase chemicals that contain the required constituents. Structure-property relationships are the key features of electronic devices and basis of thin film technologies. Underlying the performance and economics of thin film components are the manufacturing techniques on a specific chemical reaction. Thus chemical reactions may depend on thermal effects, as in vapor phase deposition and thermal growth. However, in all these cases a definite chemical reaction is required to obtain the absolute film.

A classification scheme is presented in Table 1 where we have grouped thin-film deposition technologies according to evaporative glow discharge, gas-phase chemical, and liquid-phase chemical processes.

Table 1. Classification of Thin-Film Deposition Technologies

* Physical Vapor Deposition

a. Evaporative Methods:

• Vacuum Evaporation

Conventional vacuum evaporation (Thermal)
Electron-beam evaporation
Molecular-beam epitaxy (MBE)
Pulsed laser evaporation

b. Glow –Discharge Processes:

• Sputtering

Diode sputtering
Reactive sputtering
Bias sputtering (ion plating)
Magnetron sputtering
Ion beam deposition
Ion beam sputter deposition
Reactive ion plating
Cluster beam deposition (CBD)

• Plasma Processes

Plasma-enhanced CVD
Plasma oxidation
Plasma anodization
Plasma polymerization
Plasma nitridation
Plasma reduction
Microwave ECR plasma CVD
Cathodic arc deposition

Gas-Phase Chemical Processes

* Chemical Vapor Deposition (CVD) Processes

CVD epitaxy
Atmospheric-pressure CVD (APCVD)
Low-pressure CVD (LPCVD)
Metalorganic CVD (MOCVD)
Photo-enhanced CVD (PHCVD)
Laser-induced CVD (LICVD)
Electron-enhanced CVD

• Thermal Forming

Thermal oxidation
Thermal nitridation
Thermal polymerization

Ion implantation

Liquid-Phase Chemical Techniques

• Electro Processes

Electroplating
Electroless plating
Electrolytic anodization
Chemical reduction plating
Chemical displacement plating
Electrophoretic deposition

• Mechanical Techniques

Spray pyrolysis
Spray-on techniques
Spin-on techniques

Liquid phase epitaxy

4. Overview of Various Thin Film Deposition Technologies:

A brief description of the principles, salient features and applications for some of the important thin-film deposition processes are given below.

Physical Vapor Deposition (PVD):

PVD refers to the process where solid material to be deposited is physically converted to vapor phase. The vapor phase is transported across a region of reduced pressure from the source to the substrate, at which film growth proceeds. Structural improvement of the film requires migration of arriving species on the growth surface and there is a need to balance arrival rate with this surface mobility, allowing time for atoms to reach equilibrium sites.

4.1 Evaporative Technologies:

One of the oldest techniques used for depositing thin films, thermal evaporation or vacuum evaporation is still widely used in the laboratory and in industry for depositing metal and metal alloys. The following sequential basic steps take place: (*i*) a vapor is generated by boiling or subliming a source material (*ii*) the vapor is transported from the source to the substrate and (*iii*) the vapor is condensed to a solid film on the substrate surface. Evaporates cover an extraordinary range of varying chemical reactivity and vapor pressures.

This variety leads to a large diversity of source components including resistance heated filaments, electron beams; crucibles heated by conduction, radiation, or rf-induction; arcs, exploding wires, and lasers. Additional complications include source-container interactions, requirements for high vacuum, precise substrate motion (to ensure uniformity) and the need for process monitoring and control.

In the process of evaporation, heat is enter into the source material (often called the charge, which may be an elemental metal, an alloy, a mixture or a compound) to create a plume of vapor which travels in straight line paths to the substrate. The atoms, molecules, and clusters of molecules condense from the vapor phase to form a solid film, upon arrival at the substrate. The heat of condensation is absorbed by the substrate.

On a microscopic scale the localized heating from this process can be huge. In the development of metal coating techniques for thin cross section plastic parts, it is common, to melt substrates during the initial deposition runs. Monitoring of source-to-substrate distances and deposition rates will allow coating of temperature sensitive substrates without melting.

There are several methods by which heat can be delivered to the charge to cause vaporization: induction heating, electric resistance heating, and electron beam heating. Deposition of thin films by laser ablation and cathodic arc could be grouped in this section with thermal processes.

The laser source is located outside the evaporation system and the beam penetrates through a window and is focused on to the evaporate material, which is generally fine powder form.

Thermal evaporation:

Thermal evaporation is a common method of thin-film deposition. The source material is evaporated in a vacuum. The vacuum allows vapor particles to travel directly to the target object (substrate), where they condense back to a solid state.

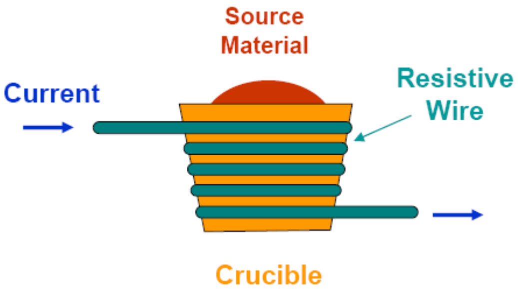
Thermal evaporation is used in micro-fabrication to make electrical contacts. In thermal evaporation resistive coil or boat is used that contains charge in solid bar or powder form. A large DC current passed through resistive coil/boat to acquire high melting points of respective metals, where metal get evaporated and attain to substrate in high vacuum conditions.

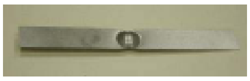
The low melting points materials can be deposited by this technique specially. A type of resistive/boat heaters is as shown in figure (a).

Evaporation takes place in a vacuum, i.e. vapors other than the source material are almost entirely removed before the process begins.

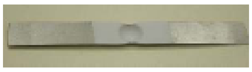
The thermal evaporation chamber is pumped by diffusion pump to create high vacuum. The material that is to be deposited is placed in heater or the crucible that is heated by giving DC power supply.

As the crucible or heater gets heated the charge gives off vapor that reaches to substrate and sticks on the surface. In high vacuum (with a long mean free path), evaporated particles can travel directly to the deposition target without colliding with the background gas. Hot objects in the evaporation chamber, such as heating filaments, produce unwanted vapors that limit the quality of the vacuum. The schematic of thermal evaporation system is shown in figure (b).

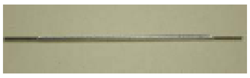




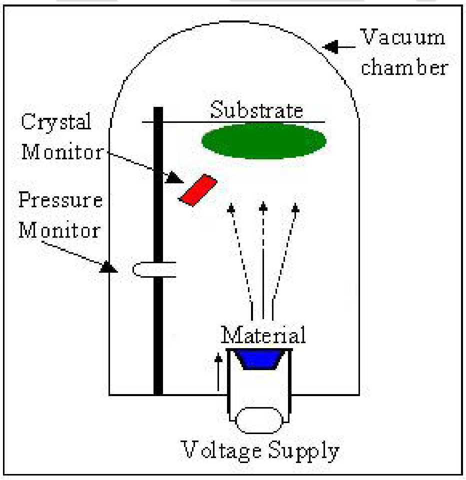
Foil Dimple Boat



Alumina Coated
Foil Dimple Boat



Cr Coated Tungsten Rod



Schematic of thermal evaporation.

The issues with conventional evaporation are:

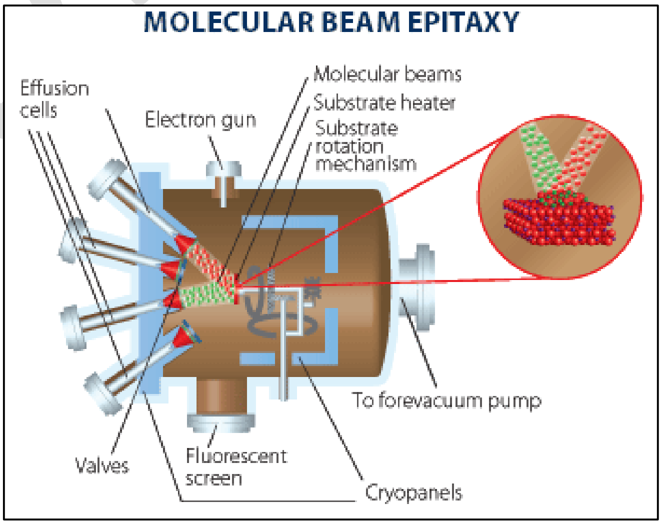
* Purity of the deposited film depends on the quality of the vacuum, and on the purity of the source material.

* At a given vacuum pressure the film purity will be higher at higher deposition rates as this minimizes the relative rate of gaseous impurity inclusion.

* The thickness of the film will vary due to the geometry of the evaporation chamber. Collisions with residual gases aggravate non-uniformity of thickness.
* Wire filaments for evaporation cannot deposit thick films, because the size of the filament limits the amount of material that can be deposited.
* In order to deposit a material, the evaporation system must be able to melt it.
This makes refractory materials such as tungsten hard to deposit by methods that do not use electron-beam heating.

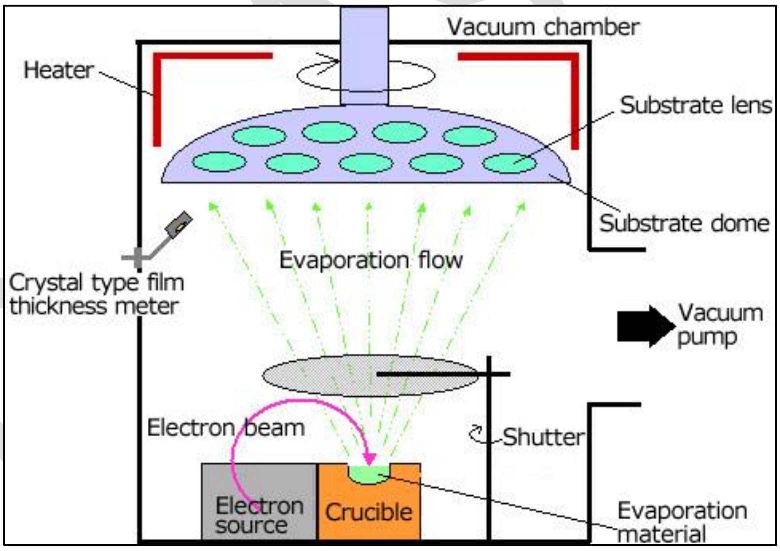
- **Molecular Beam Epitaxy:**

MBE is a sophisticated, finely controlled method for growing single-crystal epitaxial films in a high vacuum. The films are formed on single-crystal substrates by slowly evaporating the elemental or molecular constituents of the film from separate Knudsen effusion source cells (deep crucibles in furnaces with cooled shrouds) onto substrates held at a temperature appropriate for chemical reaction, epitaxy, and re-evaporation of excess reactants.
The furnaces produce atomic or molecular beams of relatively small diameter, which are directed at the heated substrate, usually silicon or gallium arsenide. Fast shutters are interposed between the sources and the substrates. By controlling these shutters, one can grow super lattices with precisely controlled uniformity, lattice match, composition, dopant concentrations, thickness, and interfaces down to the level of atomic layers.



- **Electron Beam Evaporation:**

In electron beam evaporation (EBE) a stream of electrons is accelerated through fields of typically 5–10kV and focused onto the surface of the material for evaporation. The electrons lose their energy very rapidly upon striking the surface and the material melts at the surface and evaporates. That is, the surface is directly heated by impinging electrons, in contrast to conventional heating modes. Direct heating allows the evaporation of materials from water-cooled crucibles. Such water-cooled crucibles are necessary for evaporating reactive and in particular reactive refractory materials to avoid almost completely the reactions with crucible walls. This allows the preparation of high purity films because crucible materials or their reaction products are practically excluded from evaporation. Electron beam guns can be classified into thermionic and plasma electron categories. In the former type the electrons are generated thermionically from heated refractory metal filaments, rods or disks. In the latter type, the electron beams are extracted from plasma confined in a small space.



Advantages and disadvantages

1. The deposition rate in this process can be as low as 1 nm per minute to as high as few micrometers per minute

2. The material utilization efficiency is high relative to other methods and the process offers structural and morphological control of films

3. It creates less surface damage from the imp ringing atom as the film is being formed,

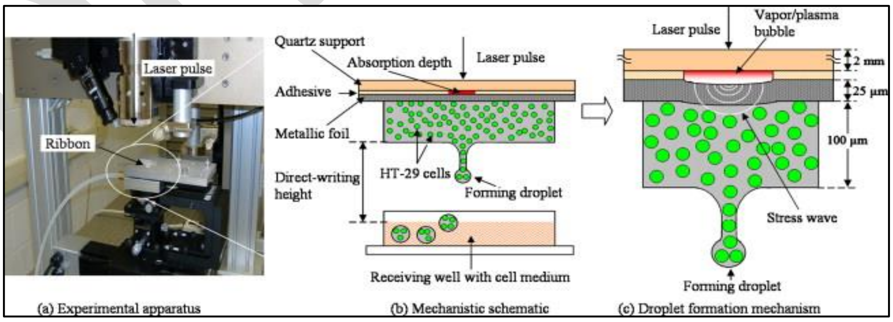
4. The film created has high purity form (due to the high vacuum area) and has less chance for the wafer (substrate) to be heated unintentionally.

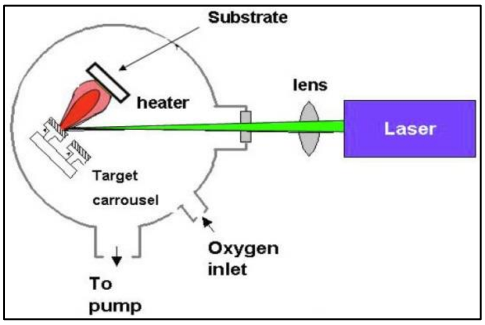
5. Electron-beam evaporation allows tight control of the evaporation rate. Thus, an electron-beam system with multiple beams and multiple sources can deposit a chemical compound or composite material of known composition.

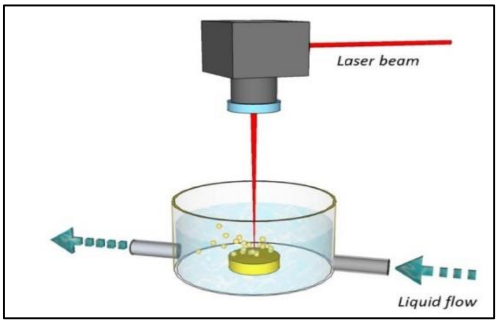
As for the disadvantage, it is more difficult to be controlled incapable of doing surface cleaning, harder to improve the step coverage and could cause x-ray damages by the electron beam evaporation.

- **Laser Induced Evaporation/Laser Ablation/Pulsed Laser Deposition (PLD).**

This technique with many names was first used by Smith and Turner in 1965 to deposit thin films in a vacuum chamber using a pulsed ruby laser. In this technique, material is vaporized and ejected from the surface of a target as it irradiated by a laser beam. Films are formed by condensing the material ablated from the target onto a solid substrate. Absorption characteristics of the material to be evaporated determine the laser wavelength to be used. To obtain the high power density required in many cases, pulsed laser beams are generally employed. Pulse width, repetition rate, and pulse intensity are selected for specific applications.







Advantages of vacuum evaporation:

*High-purity films can be deposited from high-purity source material.

* Source of material to be vaporized may be a solid in any form and purity.

* The line-of-sight trajectory and "limited-area sources" allow the use of masks to define areas of deposition on the substrate and shutters between the source and substrate to prevent deposition when not desired.

* Deposition rate monitoring and control are relatively easy.

* It is the least expensive of the PVD processes.

Disadvantages of vacuum evaporation:

* Many compounds and alloy compositions can only be deposited with difficulty.

* Line-of-sight and limited-area sources result in poor surface coverage on complex surfaces unless there is proper fixturing and movement.

* Few processing variables are available for film property control.

* Source material use may be low.

* Large-volume vacuum chambers are generally required to keep an appreciable distance between the hot source and the substrate.

Vacuum evaporation is used to form optical interference coatings using high and low index of refraction materials, mirror coatings, decorative coatings, permeation barrier films on flexible packaging materials, electrically conducting films and corrosion protective coatings.

4.2 Glow-Discharge Technologies

The electrode and gas-phase phenomena in various kinds of glow discharges (especially rf discharges) represent a rich source of processes used to deposit and etch thin films. Creative exploitation of these phenomena has resulted in the development of many useful processes for film deposition (as well as etching).

- **Sputtering:**

The most basic and well-known of these processes is sputtering, the ejection of surface atoms from an electrode surface by momentum transfer from bombarding ions to surface atoms. From this definition, sputtering is clearly an etching process, and is, in fact, used as such for surface cleaning and for pattern delineation. Since sputtering produces a vapor of electrode material, it is also (and more frequently) used as a method of film deposition similar to evaporative deposition. *Sputter deposition* has become a generic name for a variety of processes.

- **DC sputtering:**

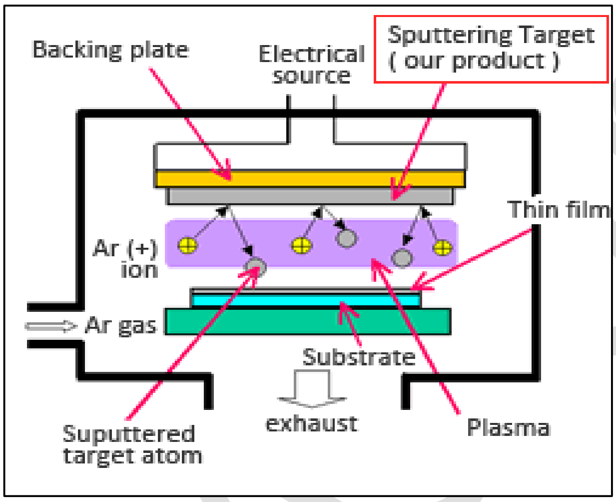
In this, D.C. electric field is impressed across two water cooled electrodes. In D.C. sputtering, it is essential that positive ions impringing on the target surface have an opportunity to recombine with electrons to avoid charge accumulation on the surface. With D.C. sputtering system, it is feasible to reverse system polarity, and thereby etch the substrate prior to film deposition. This process, known as back sputtering, is extremely useful for removing thin surface layers such as residual oxides, which can affect the electrical and mechanical properties of the film substrate combination, or prevent adhesion of the film to the substrate.

- **RF sputtering:**

Radio frequency sputtering is generally carried out with 1 to 3 kV peak to peak r.f. potential. Excitation is normally offered at 13.36 MHz, which is intentionally assigned for equipment usage. DC sputtering cannot be used for insulating films because the surface on the target becomes positively charged. The use of a RF power source with an impedance matching network solves this problem and allows the sputtering of insulating materials. The voltage applied at a frequency of 13.56 MHz; allows for charging and discharging of the insulating target.

- **Diode Sputtering:**

Diode sputtering uses a plate of the material to be deposited as the cathode (or rf-powered) electrode (target) in a glow discharge. Material can thus be transported from the target to a substrate to form a film. Films of pure metals or alloys can be deposited when using noble gas discharges (typically Argon) with metal targets.



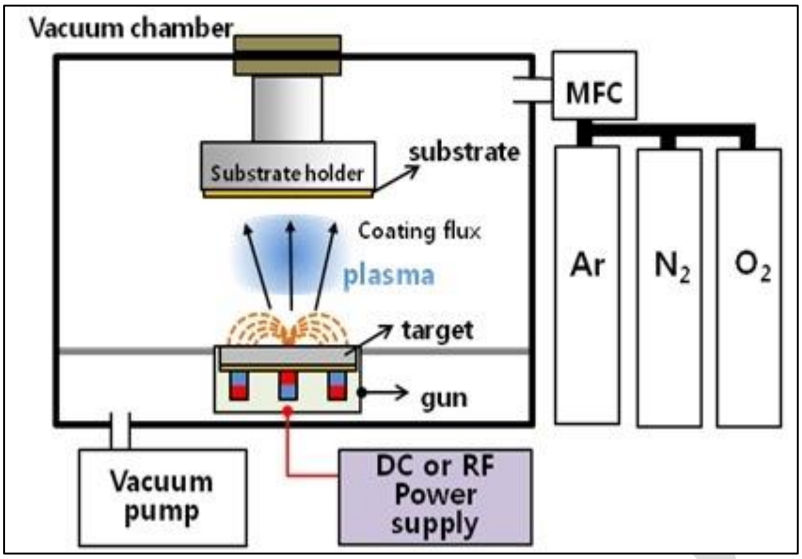
- **Reactive Sputtering:**

Compounds can be synthesized by reactive sputtering, that is, sputtering elemental or alloy targets in reactive gases; alternatively, they can be deposited directly from compound targets.

Reactive sputtering can be used to deposit films of such materials like oxides or nitrides through the use of pure metal targets. In addition to the sputtering gas (argon), a reactive species-oxygen or nitrogen, for example-is introduced into the growth chamber. The sputtered target atoms react with the gas to form the new material.

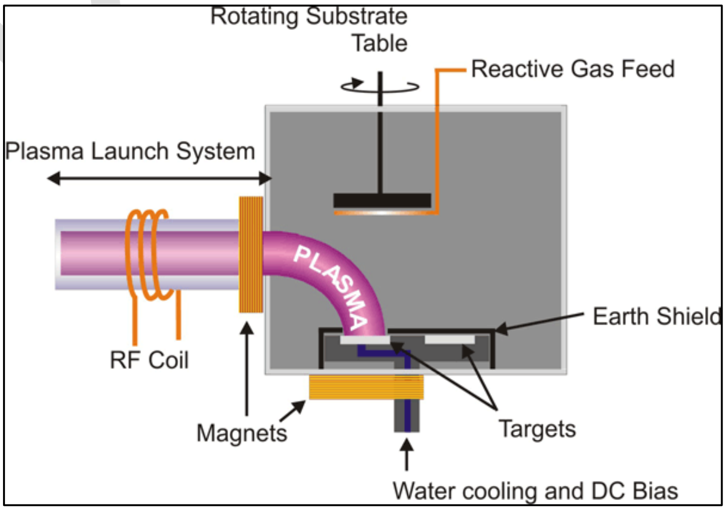
Some of the benefits of sputtering include:

1. High uniformity of thickness;
2. Good adhesion of film to substrate;
3. Reproducibility of films;
4. Ability to deposit and maintain the stoichiometry of the target material;
5. Relative simplicity of thickness control.



- **Bias Sputtering:**

Bias sputtering or ion-plating is a variant of diode sputtering in which the substrates are ion bombarded during deposition and prior to film deposition to clean them. Ion bombardment during film deposition can produce one or more desirable effects, such as re-sputtering of loosely-bonded film material, low-energy ion implantation, desorption of gases, conformal coverage of contoured surface, or modification of a large number of film properties. The source material need not originate from a sputtering target, but can be an evaporation source, a reactive gas with condensable constituents, or a mixture of reactive gases with condensable constituents and other gases that react with the condensed constituents to form compounds.

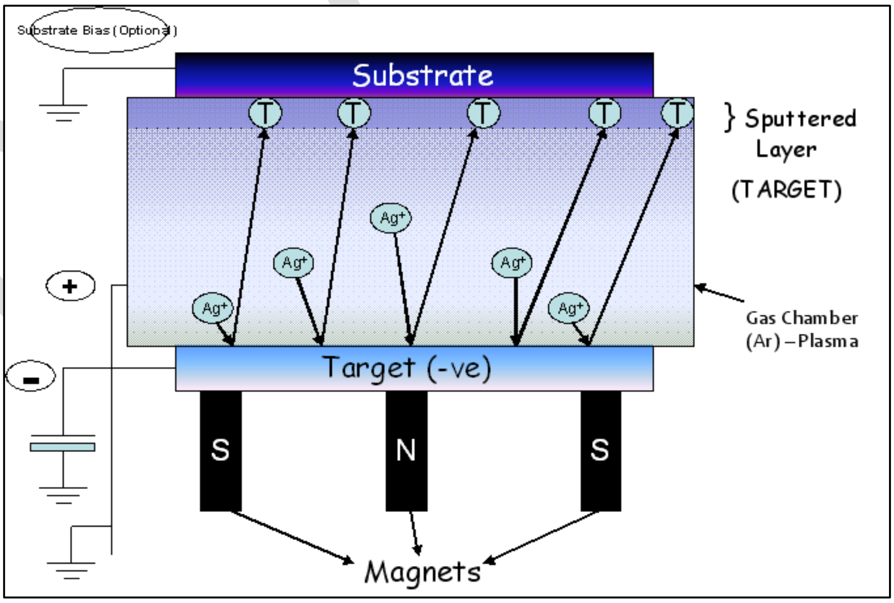


- **Magnetron Sputtering:**

Another variant in sputtering sources uses magnetic fields transverse to the electric fields at sputtering-target surfaces. This class of processes is known as *magnetron sputtering*. Sputtering with a transverse magnetic field produces several important modifications of the basic processes.

Target-generated secondary electrons do not bombard substrates because they are trapped in cycloidal trajectories near the target, and thus do not contribute to increased substrate temperature and radiation damage. This allows the use of substrates that are temperature-sensitive (for example, plastic materials) and surface sensitive (for example, metal-oxides-semiconductor devices) with minimal adverse effects. In addition, this class of sputtering sources produces higher deposition rates than conventional sources and lends itself to economic, large-area industrial application. There are cylindrical, conical, and planar magnetron sources, all with particular advantages and disadvantages for specific applications.

As with other forms of sputtering, magnetron sources can be used in a reactive sputtering mode. Alternatively, one can forego the low temperature and low radiation-damage features and utilize magnetron sources as high-rate sources by operating them in a bias-sputtering mode.

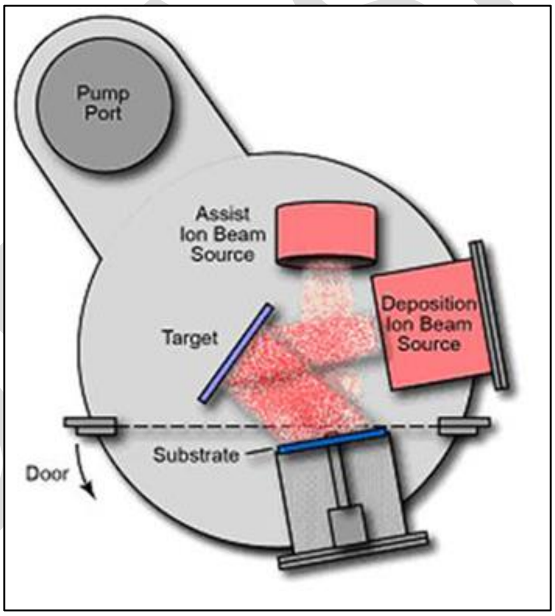


The application of magnetic field in plasma causes the electrons to spiral around the direction of the magnetic field lines. Magnetron sputtering utilizes magnetic fields to increase deposition rates and allow for low operating pressures and temperatures. For example, the application of a planar magnetron will cause electrons in the glow discharge to follow a helical path, increasing the rate of collisions and ionization. Therefore, magnetron sputtering grows high quality films at lower operating pressures.

- **Ion-Beam Sputtering:**

Ion beams, produced in and extracted from glow discharges in a differentially pumped system, are important to scientific investigations of sputtering, and are proving to be useful as practical film deposition systems for special materials on relatively small substrate areas.

There are several advantages of ion-beam sputtering deposition. The target and substrate are situated in a high-vacuum environment rather than in a high pressure glow discharge. Glow discharge artifacts are thereby avoided, and higher-purity films usually result. Reactive sputtering and bias sputtering with a separate ion gun can be used.



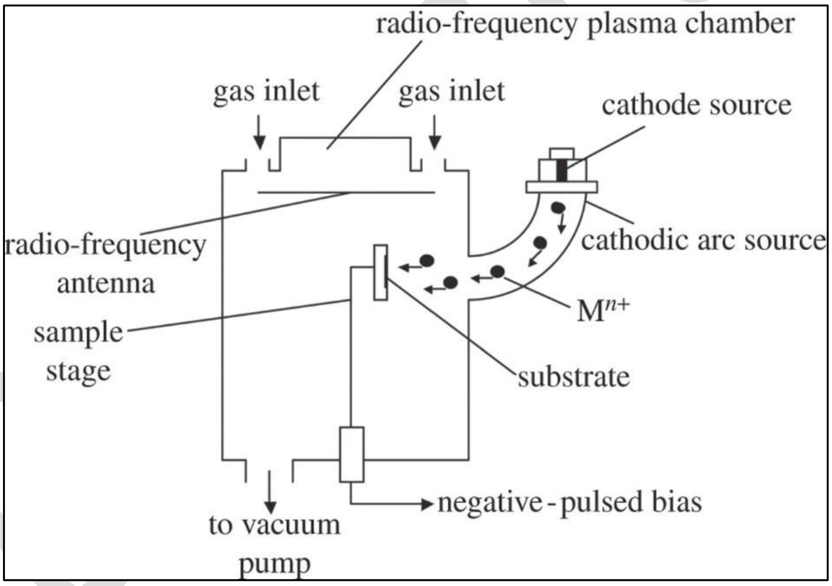
- **Plasma Processes:**

The fact that some chemical reactions are accelerated at a given temperature in the presence of energetic reactive-ion bombardment is the basis of processes for surface treatments such as plasma oxidation, plasma nitriding, and plasma carburizing. A metal to be oxidized, nitrided or carburized is made the cathode of a glow discharge and is simultaneously heated by radiant or rf-induction means. Protective coatings on a variety of metals can be produced in this way to render surfaces hard and/or corrosion resistant.

- **Anodization:**

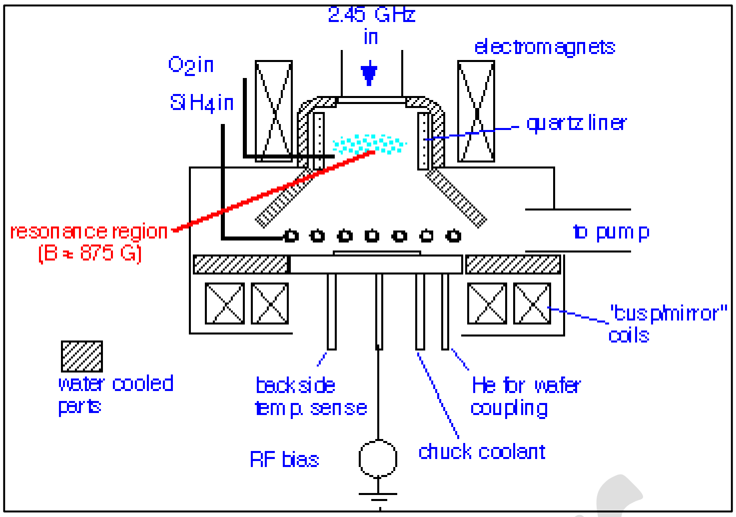
Plasma anodization is a technique for producing thin oxide films (less than 100 nm) on metals such as aluminum, tantalum, titanium, and zirconium, collectively referred as *valve metals*. In this case, a dc discharge is set up in an oxygen atmosphere and the substrates (shielded from the cathode to avoid sputter deposition) are biased positively with respect to the anode. This bias extracts negative oxygen ions from the discharge to the surface, which is also bombarded with electrons that assist the reaction.

The process produces very dense, defect-free, amorphous oxide films that are of interest as gate material in III-V compound semiconductor devices such as in microwave field-effect transistors.



- **Microwave Electron Cyclotron Resonance Deposition:**

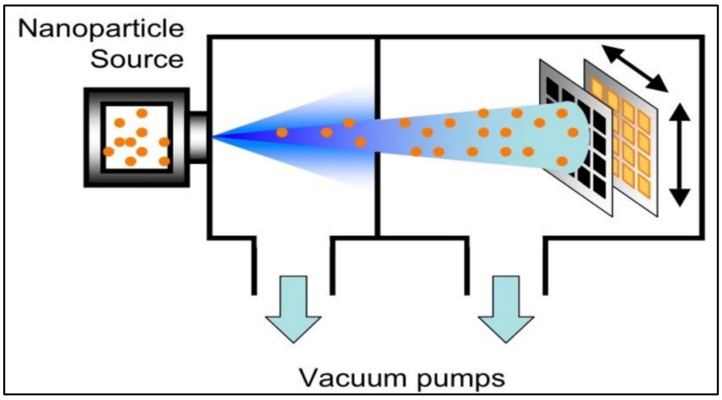
ECR plasma deposition employs an electron cyclotron resonance (ECR) ion source to create high-density plasma. The plasma is generated by resonance of microwaves and electrons through a microwave discharge across a magnetic field. The main feature of this recently introduced process is the high rate of deposition obtained at a low temperature of deposition.



- **Cluster Beam Deposition:**

Ionized cluster beam deposition (ICB) or cluster beam deposition is one of the most recent emerging technologies for the deposition of thin films with growth-control capabilities not attainable by other processes. ICB deposition is one of several techniques classified as ion-assisted thin-film formation. The material to be deposited emerges and expands into a vacuum environment from a small nozzle of a heated confinement crucible, usually constructed of high-purity graphite. The vapor pressure within the crucible is several orders of magnitude higher than the pressure of the vacuum chamber so that the expanding vapor super cools. Homogeneous nucleation results in the generation of atomic aggregates or clusters of up to a few thousand atoms held together by weak inter atomic forces. The clusters through the vacuum towards the substrate can, in part, be positively charged by impact ionization with electron beam irradiation.

Closely controlled accelerating voltages add energy to the ionized clusters which then impinge on the substrate, diffuse or migrate along the plane of the surface, and finally form a thin film of exceptional purity.



Advantages of sputter deposition:

* Elements, alloys and compounds can be sputtered and deposited.

* The sputtering target provides a stable, long-lived vaporization source.

* In some configurations, the sputtering source can be a defined shape such as a line or the surface of a rod or cylinder.

* In some configurations, reactive deposition can be easily accomplished using reactive gaseous species that are activated in plasma.

* There is very little radiant heat in the deposition process.

* The source and substrate can be spaced close together.

* The sputter deposition chamber can have a small volume.

Disadvantages of sputter deposition:

* Sputtering rates are low compared to those that can be attained in thermal evaporation.

* In many configurations, the deposition flux distribution is non-uniform, requiring moving fixturing to obtain films of uniform thickness.

* Sputtering targets are often expensive and material use may be poor.

* Most of the energy incident on the target becomes heat, which must be removed.

* In some cases, gaseous contaminants are "activated" in the plasma, making film contamination more of a problem than in vacuum evaporation.

* In reactive sputter deposition, the gas composition must be carefully controlled to prevent poisoning the sputtering target.

Sputter deposition is widely used to deposit thin film metallization on semiconductor material, coatings on architectural glass, reflective coating on polymers, magnetic films for storage media, transparent electrically conductive films on glass and flexible webs, dry-film lubricants, wear resistant coating on tools and decorative coatings.

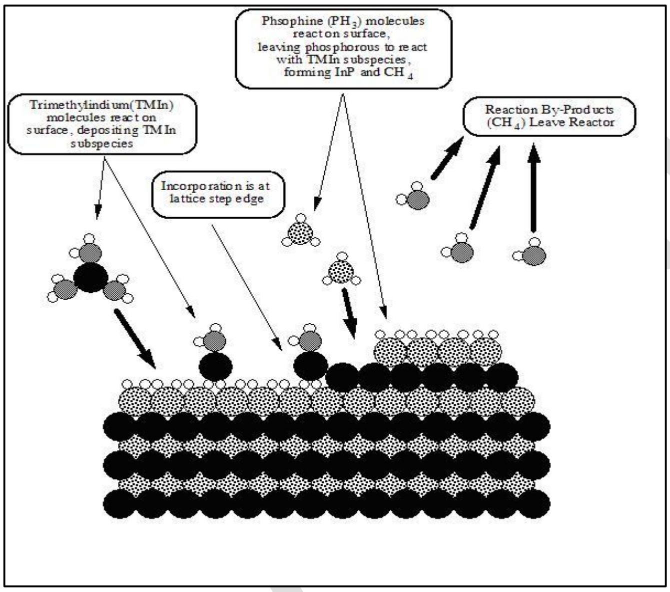
4.3 Gas-Phase Chemical Processes

Methods of film formation by purely chemical processes in the gas or vapor phases include chemical vapor deposition and thermal oxidation. Chemical vapor deposition (CVD) is a materials synthesis process whereby constituents of the vapor phase react chemically near or on a substrate surface to form a solid product. The deposition technology has become one of the most important means for creating thin films and coatings of a very large variety of materials essential to advanced technology, particularly solid-state electronics where some of the most sophisticated purity and composition requirements must be met. The main feature of CVD is its versatility for synthesizing both simple and complex compounds with relative ease at generally low temperatures. Both chemical composition and physical structure can be tailored by control of the reaction chemistry and deposition conditions.

Fundamental principles of CVD encompass an interdisciplinary range of gas-phase reaction chemistry, thermodynamics, kinetics, transport mechanisms, film growth phenomena, and reactor engineering. Chemical reaction types basic to CVD include pyrolysis (thermal decomposition), oxidation, reduction, hydrolysis, nitride and carbide formation, synthesis reactions, disproportionation, and chemical transport. A sequence of several reaction types may be involved in more complex situations to create a particular end product. Deposition variables such as temperature, pressure, input concentrations, gas flow rates and reactor geometry and operating principle determine the deposition rate and the properties of the film deposit. CVD has become an important process technology in several industrial fields. CVD has long been used for coating of substrates at reduced pressure, often at high temperatures.

- **Vapor-Phase Epitaxy:**

Vapor-phase epitaxy (VPE) and metal-organic chemical vapor deposition (MOCVD) are used for growing epitaxial films of compound semiconductors in the fabrication of optoelectronic devices. Composite layers of accurately controlled thickness and dopant profile are required to produce structures of optimal design for device fabrication.

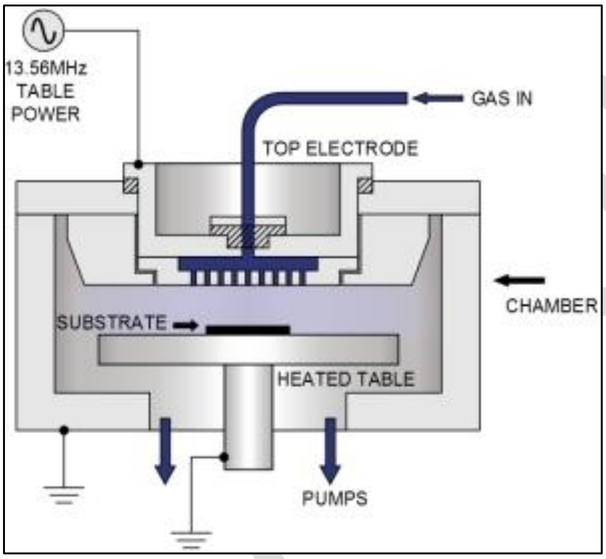


- **Photo-Enhanced Chemical Vapor Deposition (PECVD):**

PHCVD is based on activation of the reactants in the gas or vapor phase by electromagnetic radiation, usually short-wave ultraviolet radiation. Selective absorption of photonic energy by the reactant molecules or atoms initiates the process by forming reactive free-radical species that then interact to form a desired film product. Mercury vapor is usually added to the reactant gas mixture as a photosensitizer that can be activated with the radiation from a high-intensity quartz mercury resonance lamp (253.7 nm wavelength).

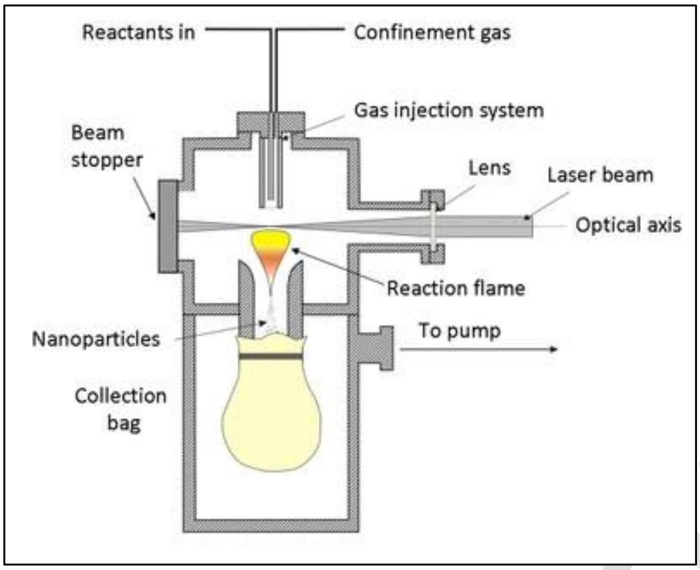
The excited mercury atoms transfer their energy kinetically by collision with the reactants to generate free radicals.

The advantages of this versatile and very promising CVD process is the low temperature (typically 150°C) needed to form films such as SiO_2 and Si_3N_4 and the greatly minimized radiation damage (compared to PECVD). The limitations at present are the unavailability of effective production equipment and the need (in most cases) for photo activation with mercury to achieve acceptable rates of film deposition.



- **Laser-Induced Chemical Vapor Deposition (LICVD):**

[LICVD] utilizes a laser beam for highly localized heating of the substrate that then induces film deposition by CVD surface reactions. Another mode of utilizing laser (or electron radiation) is to activate gaseous reactant atoms or molecules by their absorption of the specific wavelength of the photonic energy supplied. The resulting chemical gas phase reactions are very specific, leading to highly pure film deposits.



- **Ion Implantation.**

Recently, ion implantation has been used to form silicon-on-insulator structures by implanting large doses of atomic or molecular oxygen ions in single-crystal silicon substrates to produce a buried oxide layer with sharp interfaces after annealing. Simultaneous high-dose implantation of low energy oxygen and nitrogen ions into silicon yields very thin films of silicon oxynitride, whereas low-energy implantation of nitrogen or ammonia into silicon yields a low-density silicon nitride layer.

- **Thermal Oxidation.**

In the gas phase, thermal oxidation is a chemical thin-film forming process in which the substrate itself provides the source for the metal or semiconductor constituent of the oxide. This technique is obviously much more limited than CVD, but has extremely important applications in silicon device technology where very high purity oxide films with a high quality Si/SiO2 interface are required.

Thermal oxidation of silicon surfaces produces glassy films of SiO_2 for protecting highly sensitive p-n junctions and for creating dielectric layers for MOS devices. Temperatures for this process lie in the range of about 700°C to 1200°C with either dry or moist oxygen or water vapor (steam) as the oxidant. Steam oxidation proceeds at a much faster rate than dry oxidation. The oxidation rate is a function of the oxidant partial pressure and is controlled essentially by the rate of oxidant diffusion through the growing SiO_2 layer to the SiO_2/Si interface, resulting in a decrease of the growth rate with increased oxide thickness. The process is frequently conducted in the presence of hydrochloric acid vapor or vapors of chlorine-containing organic compounds. The HCl vapor formed acts as an effective impurity getter, improving the Si/SiO_2 interface properties and stability.

- **APCVD:**

APCVD is a CVD method at normal pressure i.e. atmospheric pressure which is used for deposition of doped and undoped oxides. The deposited oxide has a low density and the coverage is moderate due to a relatively low temperature. The surface reaction on the heated wafer, typically at 400°C, grew films in the 2000 to 3000 Å/min range. The low temperature simple reactor design and high wafer throughput is a big advantage of this process. APCVD suffers from poor step coverage, fast precursor flow, particle contamination, frequent cleaning.

With a better understanding of the reaction mechanisms and the injection of reactants, some of these step coverage problems could be minimized. Various new reactors have been built around these enhancements and are used today. Because of improved tools, the APCVD undergoes regeneration.

- **LPCVD:**

In LPCVD a vacuum is used. LPCVD processes enable a high conformity of almost 1. This is because of the low pressure of 10 to 100 Pa (atmospheric pressure = 100.000 Pa) which leads to a non-uniform movement of the particles. The particles dispread due to collisions and cover vertical surfaces as well as horizontal ones. The conformity is supported by a high temperature of up to 900 °C. Compared to APCVD the density and stability is very high. LPCVD is a process used in the manufacturing of the deposition of thin films on semiconductors usually ranging from a few nanometers to many micrometers. LPCVD is used to deposit a wide range of possible film compositions with good conformal step coverage.

- **MOCVD:**

MOCVD (metal organic chemical vapor deposition) is a technique that is used to deposit very thin layers of atoms onto a semiconductor wafer. In MOCVD ultra-pure gases are injected into a reactor and finely dosed to deposit a very thin layer of atoms onto a semiconductor wafer. It is used to produce single or polycrystalline thin films. It is a highly complex process for growing crystalline layers to create complex semiconductor multilayer structures.

- **PECVD:**

In this method of CVD, plasma is added in the deposition chamber with reactive gases to create the desired solid surface on the substrate. The plasma is any gas in which a significant percentage of the atoms or molecules are ionized and is energetic and disposes on the surface. The PECVD takes place at 250 to 350 °C.

Due to low temperatures the process gases cannot be decomposed thermally. The plasma is created by RF (AC) frequency or DC discharge between two electrodes, the space between which is filled with the reacting gases. Because metallization, such as aluminum, cannot be exposed to high temperatures, the PECVD is used for SiO2 and Si3N4 deposition on top of metal layers. PECVD becomes alternative that is low temperature and low pressure technique having plasma as energy input. The conformity is not as good as in LPCVD (0.6 to 0.8), however, the deposition rate is much higher (0.5 microns per minute). The process parameters like gas flow rates, power input, chamber pressure, reactor geometry, inter electrode spacing; substrate temperature etc. can be controlled to achieve the desired quality films. Advantages of PECVD include the low temperature, higher film density for higher dielectric and more compression, and ease of cleaning the chamber.

Disadvantages include the expense of the equipment and the stress of plasma bombardment.

- **ALD:**

Atomic Layer Deposition (ALD) is a modified CVD process to manufacture thin films. The process uses several gases which are led into the process chamber alternating. It is a thin film deposition technique that is based on the sequential use of a gas phase chemical process. Each gas reacts in such a way that the current surface is saturated, and therefore the reaction comes to a standstill. The alternative gas is able to react with this surface in the same way. Between the reactions of these gases the chamber is purged with an inert gas, like nitrogen or argon.

A simple ALD process could look like this:

1. self-limiting reaction at the surface with first gas
2. purging with an inert gas
3. self-limiting reaction at the surface with second gas
4. purging with an inert gas

Due to the characteristics of self-limiting and surface reactions, ALD film growth makes control at atomic scale. ALD is similar in chemistry to CVD, except that the ALD reaction breaks the CVD reaction into two half-reactions, keeping the precursor materials separate during the reaction. By keeping the precursors separate throughout the coating process, atomic layer control of film growth can be obtained as fine as ~0.1 Å (10 pm) per cycle.

Separation of the precursors is accomplished by pulsing a purge gas (typically nitrogen or argon) after each precursor pulse to remove excess precursor from the process chamber and prevent 'parasitic' CVD deposition on the substrate.

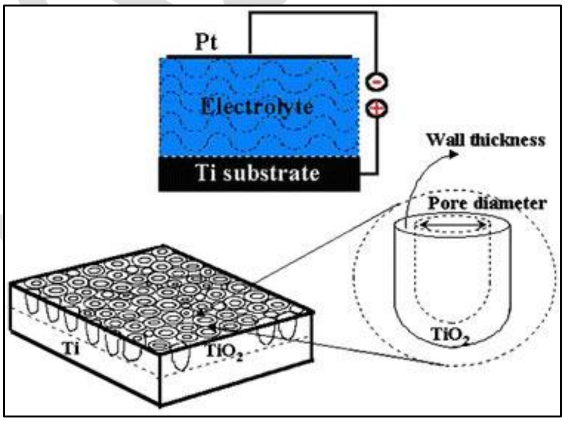
4.4 Liquid-Phase Chemical Formation

The growth of inorganic thin films from liquid phases by chemical reactions is accomplished primarily by electrochemical processes (which include anodization and electroplating), and by chemical deposition processes (which include reduction plating, electroless plating, conversion coating, and displacement deposition). A number of extensive reviews of these film formation processes discuss theory and practice. Another class of film forming methods from the liquid phase is based on chemically reacting films that have been deposited by mechanical techniques. Finally, liquid phase epitaxy is still being used for growing a number of single crystal semiconductors.

- **Electrolytic Anodization:**

In anodization, as in thermal oxidation, an oxide film is formed from the substrate. The anode reacts with negative ions from the electrolyte in solution and becomes oxidized, forming an oxide or a hydrated oxide coating on semiconductors and on a few specific metals, while hydrogen gas is evolved at the cathode.

Nonporous and well adhering oxides can be formed on aluminum, tantalum, niobium, titanium, zirconium, and silicon. The most important applications are corrosion protective films and decorative coatings with dyes on aluminum and its alloys, and layers for electrical insulation for electrolyte capacitors on aluminum and tantalum.



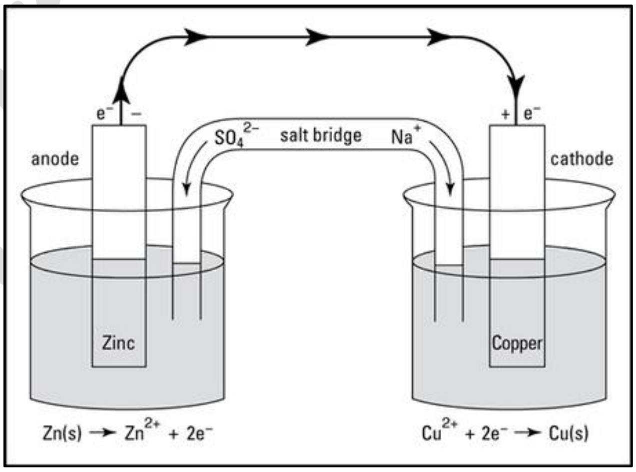
- **Electroplating:**

In electroplating a metallic coating is electrodeposited on the cathode of an electrolytic cell consisting of a positive electrode (anode), a negative electrode (cathode), and an electrolyte solution (containing the metal ions) through which electric current flows. The quantitative aspects of the process are governed by Faraday’s laws. Important electroplating variables include current efficiency, current density, current distribution, pH, temperature, agitation, and solution composition. Numerous metals and metal alloys have been successfully electroplated from aqueous solutions. Electroplating is widely used in industry and can produce deposits that range from very thin films to very thick coatings (electroforming).

- **Chemical Reduction Plating:**

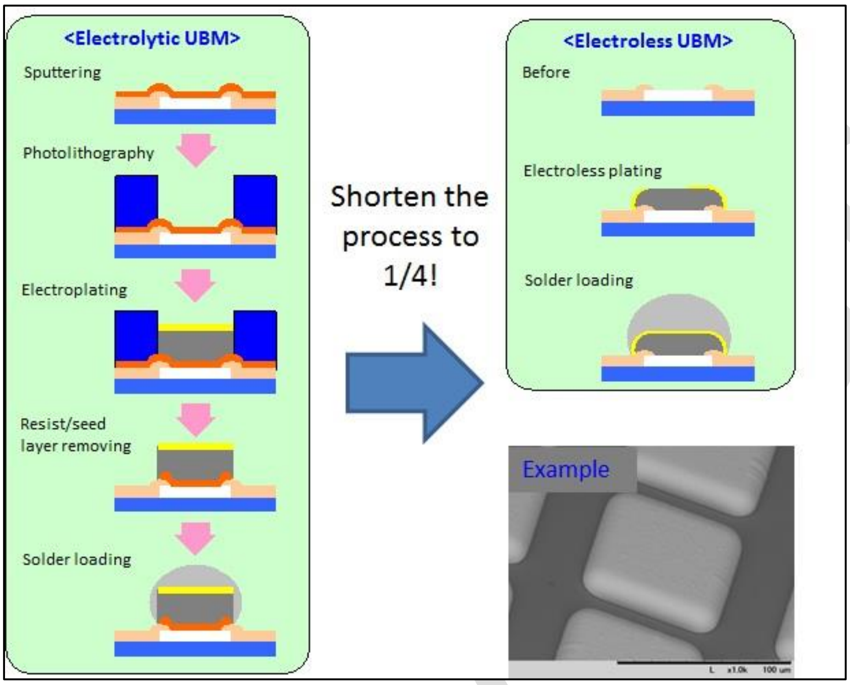
Chemical reduction plating is based on reduction of a metal ion in solution by a reducing agent added just before use. Reaction is homogeneous, meaning that deposition takes place everywhere in the solution, rather than on the substrate only.

Silver, copper, nickel, gold, and some sulfide films are readily plated. The oldest application of the process is the silvering of glass and plastics for producing mirrors using silver nitrate solutions and one of various reducing agents, such as hydrazine.



- **Electroless Plating:**

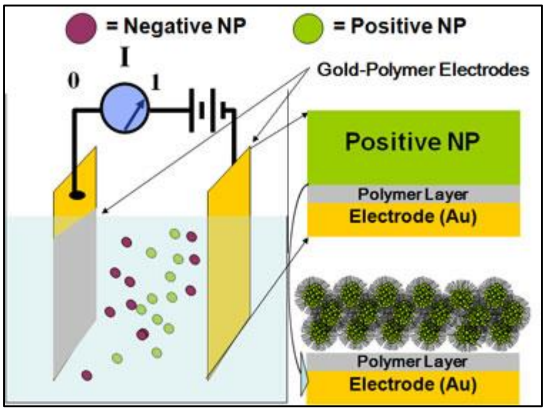
Autocatalytic or electro less plating is a selective deposition plating process in which metal ions are reduced to a metallic coating by a reducing agent in solution. Plating takes place only on suitable catalytic surfaces, which include substrates of the same metal being plated, hence the definition autocatalysis. Electroless (or electrodeless) plating offers a number of advantages over electroplating, such as selective (patterned) deposition, but is limited to a few metals and some alloys.



- **Electrophoretic Deposition:**

Electrophoretic coating is based on deposition of a film from a dispersion of colloidal particles onto a conductive substrate. The dispersion in a conductive liquid dissociates into negatively charged colloidal particles and positive ions (cations), or the reverse.

On application of an electric field between the positive substrate electrodes (anode), the colloidal particles migrate to the substrate, become discharged, and form a film.



• Immersion Plating:

Deposition of a metal film from a dissolved salt of the coating metal on a substrate by chemical displacement without external electrodes is known as displacement deposition or immersion plating. Generally, a less noble (more electronegative) metal displaces from solution any metal that is more noble, according to the electromotive force series. Actually, different localized regions on the metal surface become anodic and cathodic, resulting in thicker films in the cathodic areas. The industrial uses of this process are limited to a few applications, mainly thin coatings on copper and its alloys.