

**Module No. 6**  
**Electronic Engineering Materials**

**What is Materials?**

Common example of simple material is Clay, From clay we can make things like Earthenware, Pots, Lamps, Idols, Bricks, Roofing tile, Porcelain etc

Definition Material :*Any kind of matter from which something can be made*

**What is Engineering Materials?**

Definition Engineering Materials: *“Any kind of material which is successfully used by an engineers or technologist towards his practice or profession”*

Solid material used for engineering application in the form of

1. Bulk as regular or irregular form
2. Powder form or
3. Film or Coating form

**Role of Material Science:**

1. To investigate composition, structure, property relationship in a material and
2. To establish physical laws governing composition, structure and property of material.

**Role of material Technology:** To built the structure of a material thus producing a predetermined set of properties.

*“Material make things happen and Engineering product require material”*

**Some common functions of solid material**

1. Support loads and combat (resist) wear. This property of material required in mechanical application.
2. Insulate and conduct a) Heat b) Electricity. This property of material required in Thermal and electrical application.
3. To accept or reject magnetic flux. This property of material required in electronics, electrical, semiconductor application.
4. To transmit or reflect light. This property of material required in Optical application.
5. To survive in hostile (inconsistent/unfriendly) environment. i.e resistance to corrosion at elevated temperature. This property of material required in chemical industry application.

**Classification of Engineering Materials:**

They are classified into following types

1. Metallic Materials
2. Ceramic Materials
3. Organic Materials
4. Composite Materials
5. Electronics Materials

**1. Metallic Materials:** They provides good strength to the structure because they have properties like shearing strength, welding, casting etc.

Sub types of metallic materials are a) Pure Metals & b) its alloys

a) Metals are generally of two types

1. Ferrous
2. Nonferrous

Same way alloys are of two types

1. Ferrous
2. Nonferrous

Example of ferrous (metal) is Iron e.g. Pig iron, wrought iron, cast iron.

Example of ferrous alloys is Carbon steels & Stainless steels

Example of nonferrous Metals are Copper Zinc Nickel Gold Silver Platinum etc

Example of nonferrous Metal alloys are Brass, Bronze, Solder etc

## 2. Ceramic Materials:

Definition: These are nonmetallic inorganic solids with complex structure.

They show properties like Cohesive, adhesive & thermal resistivity

Ceramics are classified into two types

### A) On the basis of Sources

1. Natural: Obtained naturally, & used directly e.g. Abrasives, Clay, rocks, Minerals, Oxides, Cement (cohesive property), Refractory's (High thermal stability), Glass, Asbestos, Mica

2. Synthetics: Obtained by solid state reaction

e.g. 1. Clay + Lime stone (1200°C) → Portland cement, Glass, Ceramics

2.  $\text{Cu}(\text{NO}_3)_2 + \text{Ba}$  (950 °C,  $\text{O}_2$  & 24Hr) →  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  Super cond

### B) On the basis of Structural Phases

1. Crystalline ceramics – All phases or components are crystalline – e.g. Corundum

2. Amorphous ceramics - All phases or components are amorphous – e.g. Oxides

3. Mixed ceramics – Consists both crystalline and amorphous phases – e.g. Cement

4. Glass – Bears glassy structure – e.g. glass.

**C) On the basis of applications the types of ceramics are** i) Abrasives: hard & wear resistant. ii) Oxides: on solid state reaction iii) Minerals iv) Glass v) Cements: high bonding properties vi) Clay: on solid state reaction vii) Rocks/stones: used in construction/architectural purpose viii) Asbestos/Mica: Good heat & electrical insulator ix) Ceramic superconductors

## 3. Organic Materials:

These are high polymeric materials. Generally bad conductor of electricity, Plastic, High strength, Elastic, Noncorrosive etc

They are of four types a) Plastics b) Rubber c) Fibers d) Adhesives

## 4. Composite Materials:

It is made by composition of two or more different components, providing properties differ than that of the individual components.

They are of different types

1. Agglomerated composites e.g. Mosaic tile

2. Laminating composites e.g. Plywood: Layer wise composites: Layer made by floor of wood & adhesives.

3. Surface coating composites: Layer of adhesive CD, VCD, DVD, Superconducting plates, Photocells etc.

4. Reinforced composites: Regular network of one material is introduced in bulk of parent materials e.g. RCC, FRP

5. Nano Composites: Composites on atomic/ molecular level e.g. thin films

## 5. Electronics Materials:

a). Silicon based semiconductors: used in every electronic device.

b). Smart Material: They have extraordinary behavior e.g. Nitinol (Alloy of Ni & Ti) called shape memory alloy

## Introduction thin film:

Engineered materials are the future of thin film technology. Engineered structures such as super lattices, nano laminates, nanotubes, nano composites, smart materials, photonic band gap materials, molecularly doped polymeres and structured materials all have the capacity to expand and increase the functionality of thin films and coatings used in a variety of applications and provide new applications.

New advanced deposition processes and hybrid processes are being used and developed to deposit advanced thin film materials and structures not possible with conventional techniques a decade ago. For example, until recently it was important to deposit fully dense films for all applications, but now films with engineered porosity are finding a wide range of new applications.

Hybrid processes, combining unbalanced magnetron sputtering and filtered cathodic arc deposition for example, are achieving thin film materials with record hardness.

Organic materials are also playing a much more important role in many types of coating structures and applications, including organic electronics and organic light emitting devices (OLED). These materials have several advantages compared to inorganic materials, including low cost, high deposition rates, large area coverage, and unique physical and optical properties. It is also possible to molecularly dope and form nanocomposites with organic materials.

Hybrid organic/inorganic deposition processes increase their versatility, and applications that combine organic and inorganic films are increasing.

### Thin Film

A microscopically *thin layer* of material that is deposited onto a metal, ceramic, semiconductor or plastic base. Typically less than one micron thick, *thin films* can be conductive or dielectric (non-conductive) and are used in myriad(countless) applications. For example, the top metallic layer on a chip and the coating on magnetic disks.

The film properties mainly depend upon the preparative conditions, film structures, and presence of defects, impurities and film thickness. Various physical constants related to the bulk material properties may not often be the same for corresponding films prepared from the bulk.

### What is thin film?

**It is solid layer of substance /material, deposited onto supporting substrate (metal, ceramic, semiconductor or plastic base) ranging from nanometers to several micrometer in thickness, where properties of deposited material significantly different from its bulk material called thin film.**

**(Film with nano to micrometer not showing significant property change are not thin film)**

*An ideal film can mathematically be defined as 'Homogenous' solid material extended infinitely in two directions (say X and Y) restricted along the third direction (Z), perpendicular to the XY plane.*

A film may contain many imperfections, impurities, dislocations, grain boundaries and various other defects and also be discontinuous. Some of these features can be minimized by appropriate control of the deposition conditions.

Thickness plays an important role in thin films, which affects the optical, electrical, structural properties of materials considerably.

Further it may broadly be classified in three subdivisions according to its thickness as,

I) Ultra-thin (50- 100Å°)

II) Thin (100- 1000Å°)

III) Comparatively thick one (greater than 1000Å°)

**Substrate/ Wafer:** It is the base material on which thin film deposition processing is conducted.

Thin film devices and components are preferred over their bulk counterparts, because of compactness, better performance, reliability coupled with low cost of production and low package weight.

Thin films have distinct (Diverse) advantages over bulk materials. Because

- i) Most processes used to deposit thin films are non-equilibrium in nature.
- ii) The composition of thin films is not constrained by metallurgical phase diagrams.
- iii) Crystalline phase composition can also be varied to certain extent by deposition conditions.
- iv) Every property of the thin film depends on and can be modified by the deposition process.
- v) All processes do not produce materials with the same properties.

- vi) Technological properties of materials such as Microstructure, surface morphology, electrical, and optical etc. are controlled by the deposition process.
- vii) A single material can be used in several different applications and technologies. The optimum properties for each application may depend on the deposition process used.

Since not all deposition technologies yield the same properties or microstructures, the deposition process must be chosen to fit the required properties and application.

For example,

**a) Diamond-like Carbon (DLC) films:**i) It is used to reduce the coefficient of friction of a surface and improve wear resistance i.e. coating for cutting tools.

ii) It is also used in infrared optical and electronic devices.

**b) Titanium dioxide (TiO<sub>2</sub>):**i) It is widely used thin film optical material.

ii) It is also used in photo catalytic devices and self-cleaning windows,

iii) It is also applicable in hydrogen production.

**c) Zinc oxide (ZnO):**i) Thin film has an excellent piezoelectric properties.

ii) It is also used as a transparent conductive coating and spintronics applications.

**d) Silicon nitride (Si<sub>3</sub>N<sub>4</sub>):** i) It is a widely used hard optical material

ii) It is also excellent piezoelectric response.

**e) Aluminum oxide (Al<sub>2</sub>O<sub>3</sub>):**i) It is a widely used optical material

ii) It is also used in gas barriers and tribology applications.

Thin films thus offer enormous potential due to the following: (Advantages of thin films Technology)

- Creation of entirely new and revolutionary products
- Solution of previously unsolved engineering problems
- Improved functionality of existing products; engineering, medical and decorative
- Production of nano-structured coatings and nanocomposites
- Conservation of scarce (rare) materials
- Ecological considerations – reduction of effluent output and power consumption

## **Techniques of thin film depositions:**

**A) Evaporation Method:** It involves physical ejection of material as atoms or molecules & condensation or nucleation of these atoms/molecules onto a substrate.

**1. Vacuum Evaporation:** The vacuum is used to allow vapor particles to deposit directly on to the substrate.

**a) Conventional Vacuum Evaporation**

**b) Electron Beam evaporation:** Target material to be used as a coating is bombarded with an electron beam from a charged tungsten filament to evaporate and convert it to a gaseous state for deposition on the material to be coated.

**2. Molecular Beam Epitaxy (MBE):** It is an epitaxy method for thin-film deposition of single crystals and layer over layer.

**3. Reactive Evaporation:** Ionization of both the coating metal and gas atoms in the vapor phase. It is generated by when using e-beam as *evaporation* source

## **B) Glow- Discharge Processes**

**1. Sputtering:** Deposit (metal) on a surface by using fast ions to eject particles of it from a target.

**a) Diode Sputtering:** DC or Direct Current Sputtering is a Thin Film Physical Vapor Deposition (PVD) Coating technique where a target material (Cathode) to be used as the coating is bombarded with ionized gas molecules causing atoms to be “Sputtered” off into the plasma

**b) Reactive Sputtering:** The sputtered particles undergo a chemical reaction before coating the substrate

**c) Bias Sputtering (Ion plating)**

**d) Magnetron Sputtering:** In which a plasma is created and positively charged ions from the plasma are accelerated by an electrical field superimposed on the negatively charged electrode or "target"

**e) Ion beam deposition:** Ion-beam sputtering (IBS) is a method in which the target is external to the ion source

**f) Ion beam sputtering deposition:**

**g) Reactive ion plating:**

**h) Cluster beam deposition:**

## **2. Plasma Processes:**

**a) Plasma enhanced CVD:** Chemical reactions are involved in the process, which occur after creation of a plasma of the reacting gases.

**b) Plasma oxidation:**

**c) Plasma anodization:** *Plasma anodization* is an advanced technique for oxidation of semiconductor materials.

**d) Plasma Polymerization**

**e) Plasma nitridation**

**f) Plasma reduction**

**g) Microwave ECR (electron cyclotron resonance) plasma CVD :** Thin films are deposited by *microwave* electron cyclotron resonance (*ECR*) *plasma* assisted metal organic chemical vapour deposition

**h) Cathodic arc deposition:** in which an electric arc is used to vaporize material from a cathode target.

## **C) Gas Phase Chemical Processes**

**1. Chemical Vapour Deposition (CVD):** In typical CVD, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired solid deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

**a) CVD epitaxy**

**b) Atmospheric Pressure CVD (APCVD)**

**c) Low Pressure CVD (LPCVD)**

**d) Metal Organic CVD (MOCVD)**

**e) Photo enhanced CVD (PHCVD)**

**f) Laser Induced CVD (PCVD)**

**g) Electron enhanced CVD**

## **2. Thermal Forming Processes**

**a) Thermal oxidation:** The technique forces an oxidizing agent to diffuse into the wafer at high temperature and react with it.

**b) Thermal Nitridation**

**c) Thermal polymerization**

**3. Ion implantation:** Ion implantation is a low-temperature process by which ions of one element are accelerated into a solid target, thereby changing the physical, chemical, or electrical properties of the target.

## **D) Liquid phase chemical techniques**

### **1. Electro processes**

**a) Electroplating**

**b) Electro less plating:** Non-galvanic *plating* method that involves several simultaneous reactions in an aqueous solution, which occur without the use of external electrical power

**c) Electrolytic anodization:**

**d) Chemical reduction plating**

**e) Chemical displacement plating**

## **f) Electrophoretic deposition**

### **2) Mechanical techniques**

**a) Spray pyrolysis :** Precursor is sprayed in a gas as fine droplets onto a heated substrate. The solvent is evaporated or decomposes into gaseous products. The salt reacts to form a deposit generally based on oxide.

**b) Spray On techniques**

**c) Spin on techniques**

### **3) Liquid phase epitaxy**


#### **Materials for thin film:**

1. Semiconductor: Si, Ge
2. Metal: Al, Au, Ag, Cu, Ti, Pd, Pt
3. Alloys
4. Polysilicon
5. Special Material: shape memory, memory storage or gas sensing oxide i.e superconducting materials
6. Dielectric: such as  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$

#### **Thin film materials for different applications**

1. Cutting tools: TiCN, TiN, TiAlN
2. High temperature corrosion resistance: AlCr, CdCr, AlCrTiSiN, silane based
3. Catalytic coating: Zinc(1-Methylimidazol)Bis(2Ethylhexanoate)Complex
4. Tribological coatings: Hydrogenated-Carbon, Nitrogenated-Carbon, CoF, Cr/ Cr<sub>2</sub>N
5. Optical coatings: i)EMI(electromagnetic interference)RFI(radio frequency interference): metal and alloy of Sn, Zn, Cu ii)UV coating:  $\text{AlF}_3$  iii) IR transparent film:  $\text{BaF}_2$  iv) Multiprotective film:  $\text{Al}_2\text{O}_3$  v) Antireflecting coating:  $\text{CeF}_2$ ,  $\text{CeO}_2$  vi) Antireflecting on glass, plastic, jewelery:  $\text{MgF}_2$  vii) IR coating:  $\text{YF}_3$  viii) IR filters:  $\text{ZnSe}$  ix) Cold light mirror:  $\text{ZnS}$  x) Absorbing layer:  $\text{CrO}_2$  xi) Multilayerantireflecting:  $\text{Na}_5\text{Al}_3\text{F}_{14}$
6. Integrated Circuit:  $\text{SiO}_2$  for Insulator and dielectric, capacitor-N type: Phosphorous, P-Type: Boron & aluminium for connector
7. LED: AlGaAs (Red) InGaN (Blue Green) AlGaInP (Yellow) These are semiconductors
8. Dielectric Coatings:  $\text{TiO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}$ ,  $\text{SiO}_2$ ,  $\text{NdF}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{PbF}_5$
9. Electrical Conductive coatings: Iron-Chrom-aluminium, Molybd-Disilicate Metal and alloy of Al, Cu, Ag
10. Gas Sensing materials:  $\text{TiO}_2$ ,  $\text{WO}$ ,  $\text{CrTiO}$ ,  $\text{SnO}$ , Metal oxides and carbon nanotubes. Semiconductors

#### **Characteristics/ Criteria of good thin film**

- 1) Good film should have uniform thickness across surface i.e. No climbing of material from gap to one side due to migration.
- 2) Good adhesion properties. (When films atoms are coming for deposition on substrate they are energetic. They sets by loosing there K.E. Hence K.E should not so high that they displace atoms from substrate. They adhere to the surface of substrate.
- 3) Good film should have good step coverage capacity and conformal   
if substrate is like step then film should cover all surface uniformly.
- 4) Good film should be inter- connected i.e not porous and dis continuous, it will give good performance.
- 5) Good film should be non-corrosive in nature.
- 6) Good film should be economical for deposition & compatible.

## **Physical Vapour Deposition Technique (PVD):-**

**Physical vapor deposition (PVD)** describes a variety of vacuum **deposition** methods which can be used to produce thin films and coatings.

Physical vapor deposition processes are atomistic ( individual atom) deposition process in which the material is vaporized from solid or liquid source in the form of atoms or molecules, transported in the form of a vapor through a low pressure gaseous (or plasma) environment to the substrate where it condenses.

**PVD** is characterized by a process in which the material goes from a condensed phase to a **vapor** phase and then back to a thin film condensed phase.

**Principle:**It involves physical ejection of material as atoms or molecules & condensation or nucleation of these atoms/molecules onto a substrate.

This method is useful for thin film coating for

1. Semiconductor devices such as thin film **solar panels**
2. Aluminized [Polyethylene terephthalate (made from polyester, thermoplastic used in fabrics) ]**PET film for food packaging**
3. **Titanium nitride coated cutting tools** for metal working i.e for ceramic , polymers , alloys & compositions , etc.
4. **Insulators:** thermal insulation coatings
5. **Optical film** for semiconductor industries.

Typical PVD process looks like a four step process:

- 1) Conversion of condensed matter (Depositing) into condense phase.
- 2) Evaporation of condensed matter into gas phase
- 3) Transportation of gas phase into some place i.e. substrate with vacuum& inert gas molecule (Argon)
- 4) Condensation of gas phase onto substrate surface without chemical reaction.

### **Advantages of PVD -**

- 1) High deposition rates
- 2) Ease of sputtering any metal, alloy or compound
- 3) High-purity films
- 4) Extremely high adhesion of films
- 5) Excellent coverage of steps and small features
- 6) Ability to coat heat-sensitive substrates
- 7) Ease of automation
- 8) Excellent uniformity on large-area substrates

### **Different Physical vapor deposition treatments**

Various Physical vapor deposition processes have been developed to match the requirement of industrial applications regarding thin film coatings.

On the basis of energy used to agitate material into atomic/molecular state for deposition, there are so many methods out of that two methods are A) Evaporation B) Sputtering discussed below.

#### **A) Evaporation method**

Evaporation method is the simplest way to coat substrate with another material.

Principle of this method is to evaporate the material in the vicinity of the substrate and it is the basis for various techniques like **Thermal evaporation, Electron beam evaporation and Cathodic arc evaporation.**

For better quality of film by evaporation, System required

a) **Vacuum pump:** Pressure in chamber Needs  $10^{-6}$  torr, to avoid corrosion /oxidation of material in gas phase. Similarly better vacuum means high mean free path, which avoids collision between evaporant atom & inert gas in chamber as well as high vacuum allows unidirectional flow.

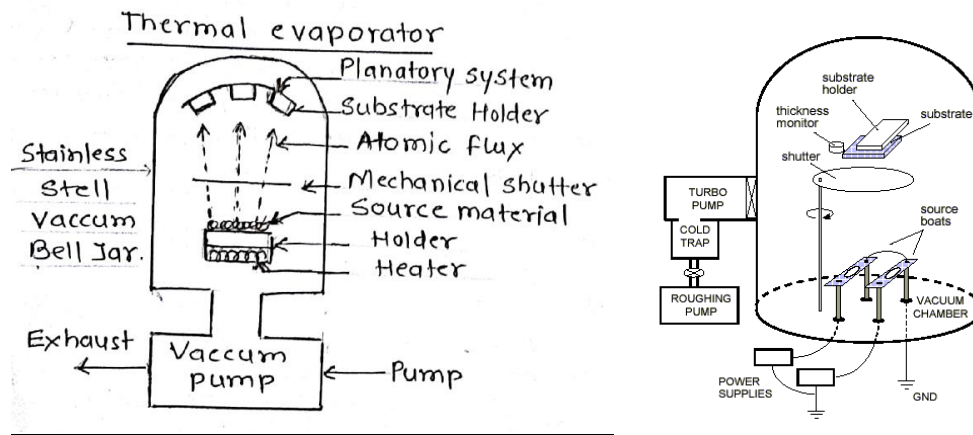
**b) Heating System:** Thermal heating / Electron beam: It converts material/Condensed matter into gas phase required 1-10 KW power

**c) A Bell-Jar:** To keep vacuum: Made from stainless steel jar, non-corrosive.

**d) Thickness monitor:** It avoids formation of thick film also very thin film i.e. to maintain appropriate thickness necessary. This is mechanical shutter system.

**1. Thermal evaporation:** In thermal evaporation, low melting materials are heated to the point of evaporation directly or by ohmically (Electric heating coil) heated containers in low pressure. The low pressure ensures the long mean free path for the evaporated atoms such that they can transit to the substrate without being scattered by ambient (inert carrier gas) gas molecules.

Material which can be evaporated by this technique are Al, Sn, Cr, Sb, Ge, In, Au, Ag, Ca, Mg (up to  $800^{\circ}\text{C}$ ) Cd, Pb, CdSe, NaCl, KCl,  $\text{MgF}_2$ ,  $\text{CaF}_2$  (self-assembled nano structures.)



### Process:

- A thermal evaporator uses an electric resistance heater to melt the source material & raises its V.P to a useful range.
- Thermal energy is important to atom in a liquid/solid source so that it can efficiently evaporate.
- Evaporation takes place in vacuum ( $10^{-6}$  Torr)
- Evaporated particles (flux) can travel directly to the deposition target without colliding with the background gas (Inert gas Ar)
- Finally deposited on substrate on atomic level.

### Advantages:

- Simple & cheap.
- Excellent purity of film
- Less surface damage of the substrate

### Disadvantages:

- Limited to low M.P metals
- Poor density & adhesion.
- Not possible to evaporate the dielectric material
- Step coverage is more difficult to improve

### Applications:

- Evaporation of metals, alloys, etc.
- Gold plating machine
- Thermal insulation coatings

## 2) Electron beam evaporation system (e-beam)

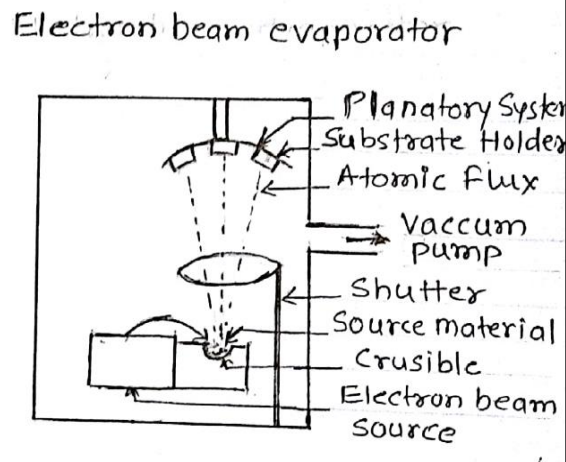
This method is particularly suitable for evaporation of high melting point material.

In Electron beam evaporation, a directed electron beam is used to cause localized melting of the material and the evaporated material leave in the same direction as the incident electron beam.



(In this system, Beam of electron bombarding onto source / precursor materials. These precursor material releasing some kind of ion, atom or molecules or plasma that deposit on base metal.)

Temperature achieved could be around  $3000^{\circ}\text{C}$ , can evaporate Ni , Pt , Ti , V , Zr , W, Mo, Rh ,  $\text{Al}_2\text{O}_3$  , SiO ,  $\text{SiO}_2$  , Titanium oxide , etc.



**Process:**

- 1) Electron beam strike on evaporating material (anode in crucible)
- 2) Coating material converted into atoms, molecules or atomic flux in gaseous state.
- 3) Atomic flux precipitate into solid form on substrate (cathode)

**Advantages:**

- 1) High (few  $\mu\text{m}/\text{min}$ ) as well as low ( $1\text{nm}/\text{min}$ ) deposition rate
- 2) Deposits high M.P materials.
- 3) Ability to control structural & morphological properties of films

**Disadvantages:**

- 1) e-beam method is complex & costlier
- 2) Extra voltage required is 5-10KV
- 3) Radiation damages substrate /human being
- 4) Heterogeneous coating may possible

**Applications:**

- 1) Aerospace material
- 2) Cutting tool
- 3) Electrical & optical film for semiconductor

Cathodic arc evaporation utilizes an electric arc to generate a localized region of extremely high temperature. The target material is vaporized as a result, and material is ejected as high velocity jet. It is then deposited at the substrate. However lack of uniformity and inability to deposit over large area substrate is the common drawback of such deposition.

**Sputtering and Sputter Deposition**

Sputtering is an etching process that alters the physical properties of a surface.

In this process, a gas plasma discharge is set up between two electrodes: a cathode plating material and an anode substrate.

The deposits are thin, ranging from  $0.00005 - 0.01\text{ mm}$ .

Chromium, titanium, aluminum, copper, molybdenum, tungsten, gold, and silver are typical deposits.

Sputter-deposited films are used routinely in decorative applications such as watchbands, eyeglasses, and jewelry.

The electronics industry relies on heavily sputtered coatings and films (e.g., thin film wiring on chips and recording heads as well as magnetic and magneto-optic recording media). Companies also use sputter deposition

to produce reflective films for large pieces of architectural glass and decorative films for plastic used in the automotive industry. The food packaging industry uses sputtering to produce thin plastic films for packaging. Compared to other deposition processes, sputter deposition is relatively inexpensive.

**Sputtering:** “Removal of atom from target material (cathode) by energy of plasma take place and deposition of that atom onto substrate (Anode) called sputtering.”

In this technique plasma which can be energized (plasma present between high voltage anode & cathode) hit the target (target is the material which you want to deposit & substrate where you want to deposit) & provide sufficient energy to stationary atom so that it will come out with moment of inversion & acceleration & hit the substrate, they loose energy & stick their, process is called sputtering.

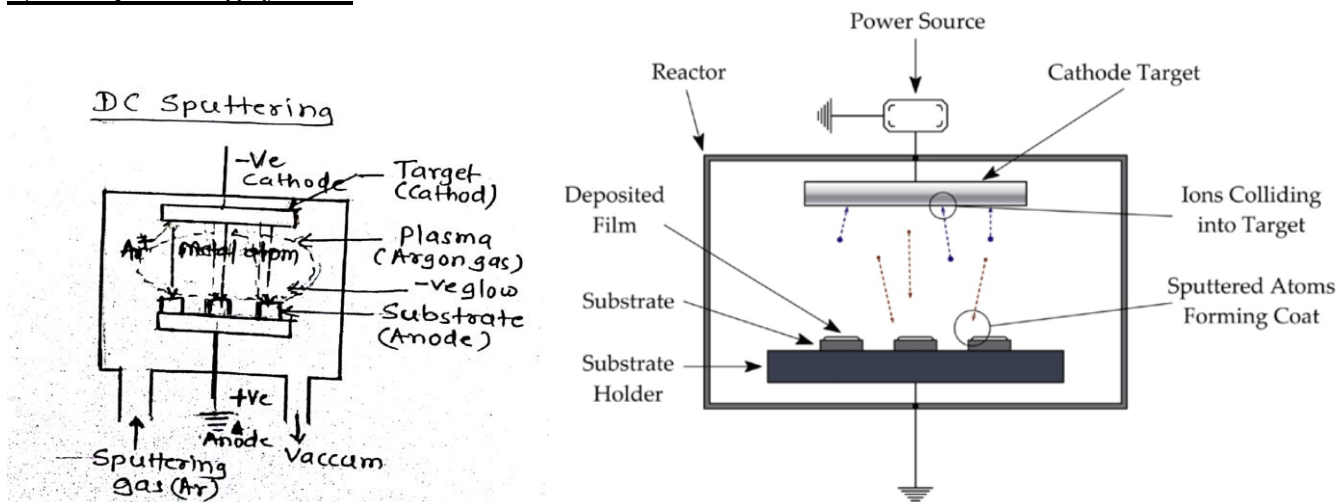
It is possible in inert as well as oxygen gas called reactive sputtering.

Metals/materials/alloys with high M.P / insulators, are normally sputtered eg: W(M.P 3300°C ) poly silicide, platinum silicide ,SiO<sub>2</sub> ,SiN , Titanium silicide .

There are two types of sputtering

- 1) DC Sputtering : This method used for metal, alloy films &
- 2) RF Sputtering : This method used for metal, alloy as well as insulators films

### 1) DC Sputtering system:



#### **Process:**

1. Target material & substrate is placed in a vacuum chamber.
2. A voltage is applied between target (cathode) & substrate (anode). Anode is ground so potential at anode is zero. Cathode have -Ve potential.
3. A plasma is created by ionizing a sputtering gas (Ar). Argon gas ions when accelerated towards cathode due to electric field and bombards cathode.
4. Atom/ molecule of target material are ejected into a gas form or plasma
5. Ejected target materials deposited onto the substrate.

#### **Advantages**

- Material having high M.P can be easily sputtered.
- Films by sputtering have a better adhesion on the substrate than evaporated films.

#### **Disadvantages**

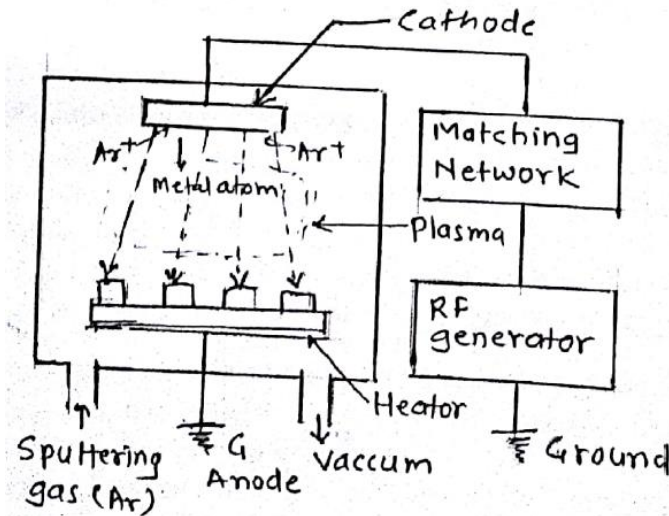
- Inert sputtering gas are built into the growing films as impurities.

### 2)Rf ( Radio Frequency) sputtering system:

Rf sputtering rarely used. It is used to deposit insulating material like SiO<sub>2</sub>, SiN.

Diagram:

## RF Sputtering



### Process:

1. Target material & substrate is placed in vacuum chamber.
2. A voltage is applied between target & substrate by **matching network** (it is variable resister provide resistance)
3. Anode is grounded so potential at anode is zero & cathode is -ve potential.
4. A plasma is created by ionizing a sputtering gas(argon)  
Argon ions when accelerated towards cathode due to electric field, bombarded cathode
5. Atoms / molecules of target material are ejected into a gas form
6. Ejected target materials deposited onto the substrate

### Advantages:

- Insulators/ dielectric can be sputtered
- Conformal deposition.

### Disadvantages:

- Energetic ions when will be heated energy of that ions should not be greater than binding energy of depositing substance otherwise breaking of molecule takes place. Eg:  $\text{SiO}_2$  want to deposit it will deposit like Si &  $\text{O}_2$  separately.

### Comparison between Evaporation& sputtering process:

Evaporation Process	Sputtering Process
Using low energy atoms (0.1ev)	Using high energy atoms(1-0.1ev)
Less denser films	More denser films
No smaller grain size	Smaller grain size
Less adhesion	Better adhesion
Takes place in high vacuum	Takes place even in low vacuum
Directional in nature	Poor directionality

Less step coverage	Better step coverage
Lower impurities	Gas atoms implanted in the films
It is with point source	It is with parallel plate source
Poor uniformity	Better uniformity
Component evaporate at different rate	All components sputtered with similar rate
Poor stoichiometry	Maintain stoichiometry

Issues in Thin Film Deposition •Quality:–Composition–Defect density (e.g. pinholes)–Contamination–Mechanical, optical, and electrical properties–Good adhesion–Minimum stress  
Topography–Uniform thickness on non-planar surfaces–Step coverage–Conformal coverage: uniform–Space filling in holes, channels–Voids  
Materials are evaporated from heated crucible (resistance heating). •Suitable for high vapor pressure metals, e.g. Au, Al,... •Good for organic materials (organic semiconductors...) • Major issues High contamination: the crucible is heated as well. On the contrary, e-beam evaporation heats only the evaporate material from the top. Can hardly work on composite films due to missing compositions

## **2. Chemical Vapour Deposition Processes**

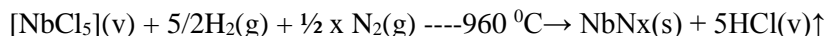
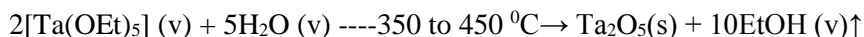
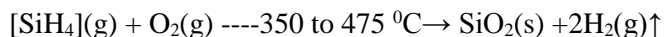
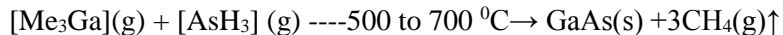
### **Conventional CVD Processes**

**CVD** is a vacuum deposition method used to produce high quality, high-performance, solid materials. The process is often used in the semiconductor industry to produce thin films.

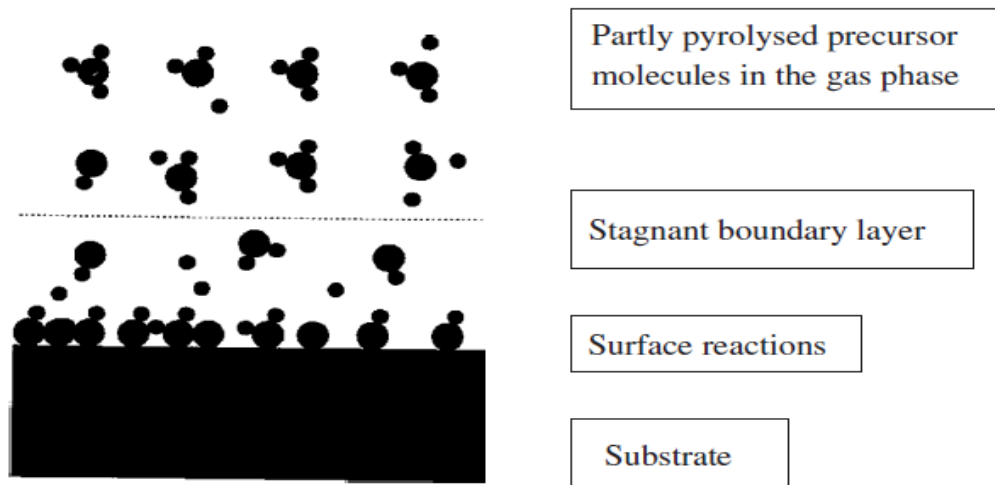
In typical CVD, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired solid deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

The resulting solid material is in the form of thin film of powder or single crystal

CVD processes are extremely complex and involve a series of gas-phase and surface reactions. They are often summarized, though, by overall reaction schemes, as illustrated in below reaction. An overall reaction scheme tells us little about the physicochemical processes and the gas-phase and surface reactions involved.

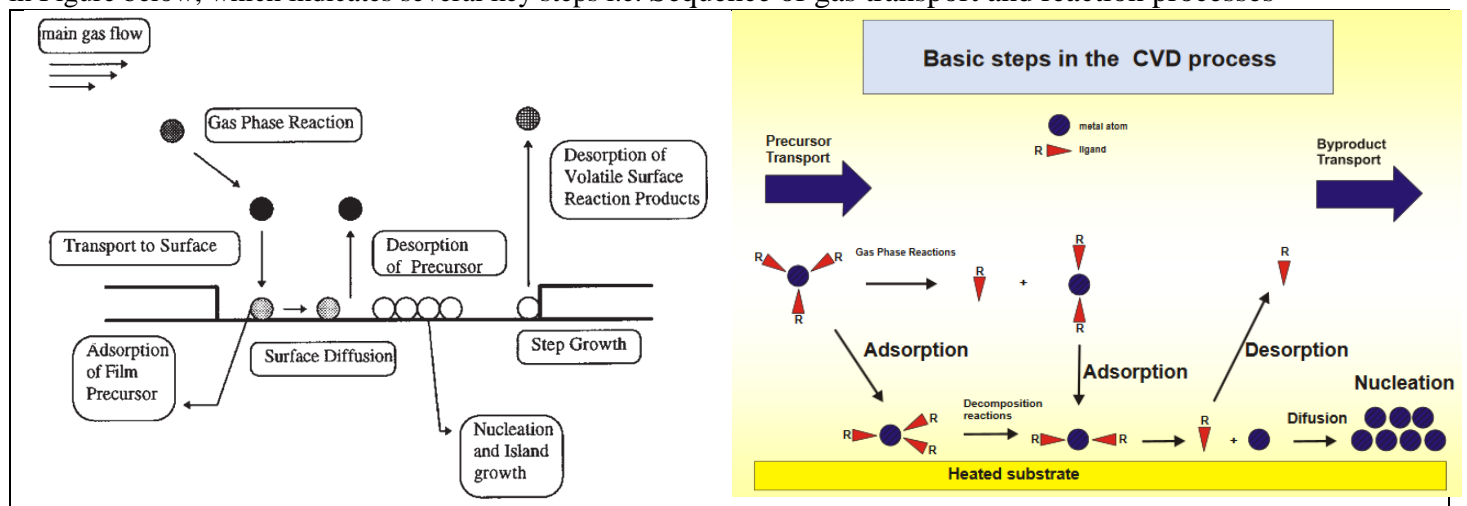


A more informative illustration of a CVD process is illustrated by the simple schematic for an CVD reaction carried out at moderate pressures (e.g. 10–760 Torr) shown in Figure



A significant feature of the process is the presence of a hot layer of gas immediately above the substrate, termed the “boundary layer”, and at these pressures gas-phase pyrolysis reactions occurring in the layer play a significant role in the CVD deposition process.

A more detailed picture of the basic physicochemical steps in an overall CVD reaction is illustrated in Figure below, which indicates several key steps i.e. Sequence of gas transport and reaction processes



1. Evaporation and transport of reagents (i.e. precursors) in the bulk gas flow region into the reactor;
2. Gas phase reactions of precursors in the reaction zone to produce reactive intermediates and gaseous by-products;
3. Mass transport of reactants to the substrate surface;
4. Adsorption of the reactants on the substrate surface;
5. Surface diffusion to growth sites, nucleation and surface chemical reactions leading to film formation;
6. Desorption and mass transport of remaining fragments of the decomposition away from the reaction zone.

OR

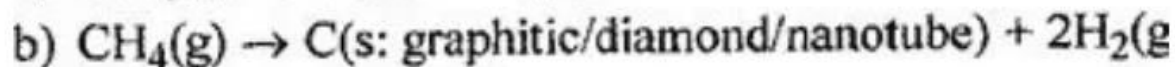
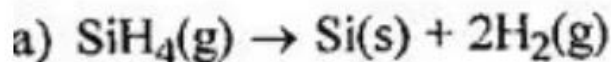
A basic CVD process consists of the following steps: 1) a predefined mix of reactant gases and diluent inert gases are introduced at a specified flow rate into the reaction chamber; 2) the gas species move to the substrate; 3) the reactants get adsorbed on the surface of the substrate; 4) the reactants undergo chemical reactions with the substrate to form the film; and 5) the gaseous by-products of the reactions are desorbed and evacuated from the reaction chamber.

The characteristics of an “ideal” CVD precursor can be summarized as follows:

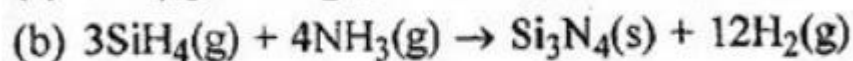
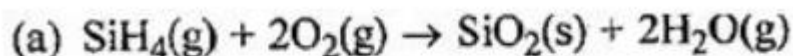
1. Adequate volatility to achieve acceptable growth rates at moderate evaporation temperatures.
2. Stability so that decomposition does not occur during evaporation.

3. A sufficiently large temperature “window” between evaporation and decomposition for film deposition.
4. High chemical purity.
5. Clean decomposition without the incorporation of residual impurities.
6. Good compatibility with co-precursors during the growth of complex materials.
7. Long shelf-life with indefinite stability under ambient conditions, i.e. unaffected by air or moisture.
8. Readily manufactured in high yield at low cost.
9. Non-hazardous or with a low hazard risk.

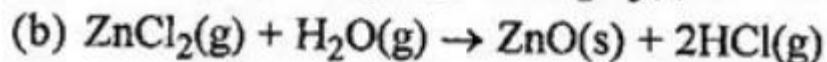
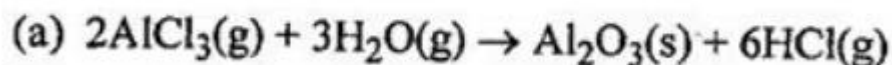
• *Pyrolysis-*



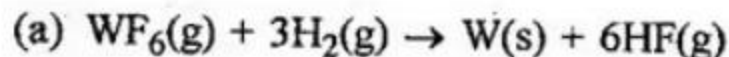
• *Oxidation-*



• *Hydrolysis-*

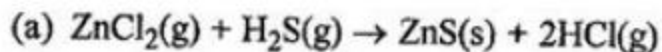


• *Reduction -*



• *Displacement -*

•



•

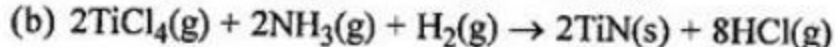
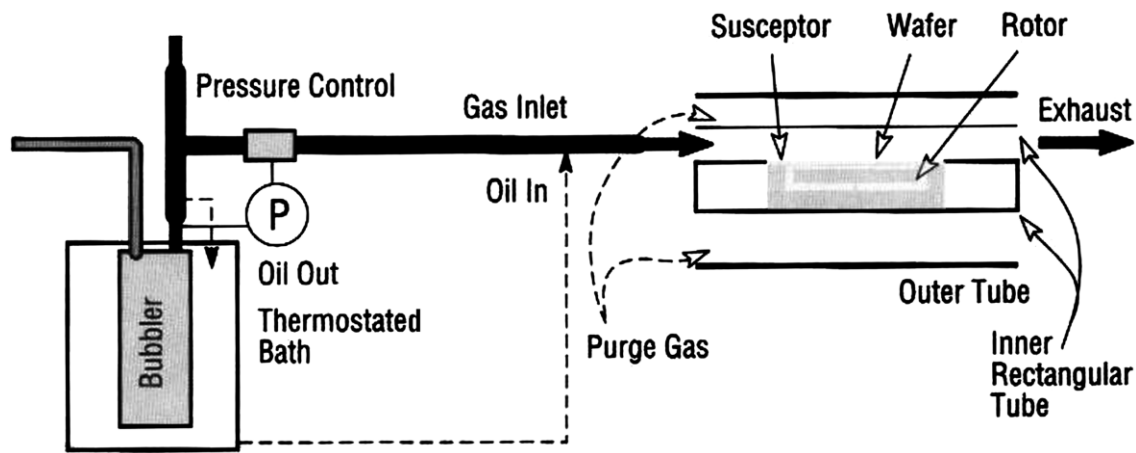


Figure 3 Schematic of a conventional MOCVD (Metal Organic CVD) reactor with a heated delivery line used to deposit ferro electric oxides [e.g.  $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ] using low vapour pressure precursors.



Applications - A very extensive range of materials has been deposited using conventional CVD and its variants.

These materials find applications in the following main areas of technology:

Microelectronics, Optoelectronics, Protective and decorative coatings, Optical coatings. As illustrated below.

#### Selection of films grown by CVD, their applications and typical precursors used.

General class of Material	Specified Materials	Applications	Typical CVD precursors
Ferroelectric oxides	$\text{SrTiO}_3$ , $(\text{Ba,Sr})\text{TiO}_3$ , $\text{Pb}(\text{Zr,Ti})\text{O}_3$ , $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{1-x})_2\text{O}_9$ , $\text{BiTiO}_{12}$ , $\text{Pb}(\text{Sc,Ta})\text{O}_3$ , $\text{Pb}(\text{Mg,Nb})\text{O}_3$	DRAMs (dynamic RAM), NVFERAM (Non-Volatile Random Access Memory), Computer Memory, Micro electromechanical devices (Used for telecommunication such as RF filter, Transistor) Transducers (device that converts energy from one form to another Tape/Disc read write head, hall effect sensor read magnetic field strength) Ceramic capacitors (A ceramic capacitor is a fixed-value capacitor where the ceramic material acts as the dielectric)	Metal- $\beta$ - diketonates ( $[\text{Ba}(\text{thd})_2]$ , $[\text{Sr}(\text{thd})_2]$ , $[\text{Ti}(\text{oPr})_2(\text{thd})_2]$ , $[\text{Bi}(\text{thd})_3]$ , $[\text{Pb}(\text{thd})_2]$ , $[\text{Sc}(\text{thd})_3]$ , $[\text{Mg}(\text{thd})_2] + \text{O}_2$ (The presence of fluorine in the 1-diketonate results in the complexes decomposing to barium fluoride. Barium fluoride is thermally stable below $1000^\circ\text{C}$ and the MOCVD of in situ superconducting $\text{YBaCuO}$ and $\text{TlBaCaCuO}$ thin films requires a non-fluorine containing complex.) Metal alkoxides ( $[\text{Bi}(\text{OR})_3]$ , $[\text{Ta}(\text{OR})_5]$ , $[\text{Nb}(\text{OR})_5]$ ) $+ \text{O}_2$ (thin films showed potentially larger polarizations with no preferred orientation at low temperatures)
General class of Material	Specified Materials	Applications	Typical CVD precursors
Ferrites	$(\text{NiZn})\text{Fe}_2\text{O}_4$ , $(\text{Mn,Zn})\text{Fe}_2\text{O}_3$	Recording Media, High frequency read heads	Metal- $\beta$ - diketonates ( $[\text{Ni}(\text{thd})_2]$ , $[\text{Zn}(\text{thd})_2]$ , $[\text{Mn}(\text{thd})_2]$ , $[\text{Fe}(\text{thd})_3]$ ) $+ \text{O}_2$ $\text{Ni}(\text{thd})_2$ : bis(2,2,6,6-tetramethylheptane-3,5-dionato)nickel(II)
General class of Material	Specified Materials	Applications	Typical CVD precursors

Dielectric Oxides	TiO <sub>2</sub> , ZrO <sub>2</sub> , ZrSi <sub>x</sub> O <sub>y</sub> , HfO <sub>2</sub> , HfSi <sub>x</sub> O <sub>y</sub>	High-k gate dielectric layers in CMO RAM (Complementary Metal Oxide Semiconductor Random Access Memory)	Metal-β- diketonates (e.g [M(β-dik) <sub>4</sub> ](M=Zr,Hf) (The use of volatile β- <b>diket</b> onate chelates as precursors for the deposition of thin films for electroluminescent devices is reviewed. Alternating current thin film electroluminescent (ACTFEL) devices consist of an emitting layer sandwiched between two dielectric layers) [Ln(OR) <sub>3</sub> ][Ln(β-dik) <sub>3</sub> ] (Ln=Lanthanide) + O <sub>2</sub> /O <sub>3</sub>
	Ln <sub>2</sub> O <sub>3</sub> , LnSi <sub>x</sub> O <sub>y</sub> , LnAlO <sub>3</sub>	Dielectric capacitor layer in DRAMs	Metal alkoxide, (e.g. [M(OR) <sub>4</sub> ] (M= Si,Ti,Zr,Hf) (M(OR) <sub>5</sub> ] (M=Ta,Nb) + O <sub>2</sub> /O <sub>3</sub> , where OR = OC <sub>n</sub> H <sub>2n+1</sub>
	SiO <sub>2</sub> , Ta <sub>2</sub> O <sub>5</sub> , Nb <sub>2</sub> O <sub>5</sub>	Dielectric capacitor layer in DRAMs Optical coatings	Metal alkyl amides [M(NR <sub>2</sub> ) <sub>4</sub> ] M= Ti,Zr,Hf) +O <sub>2</sub> /O <sub>3</sub> (Metal amide complex=NR)
<b>General class of Material</b>	<b>Specified Materials</b>	<b>Applications</b>	<b>Typical CVD precursors</b>
Conducting Oxides	(La,Sr)CoO <sub>3</sub> , (La,Mn)O <sub>3</sub> , RuO <sub>2</sub> , SrRuO <sub>3</sub>	Ferroelectric capacitor electrode	Metal - β- diketonates + O <sub>2</sub> , [Ru <sub>3</sub> (CO) <sub>12</sub> ], [Ru(β-dik) <sub>3</sub> ],[Ru(RCp) <sub>2</sub> ] (R=H,Et)
<b>General class of Material</b>	<b>Specified Materials</b>	<b>Applications</b>	<b>Typical CVD precursors</b>
Garnet(Rope)	Y <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	Microwave elements, Magneto-optics recording	Metal - β- diketonates + O <sub>2</sub>
<b>General class of Material</b>	<b>Specified Materials</b>	<b>Applications</b>	<b>Typical CVD precursors</b>
Elemental semiconductors	Si Doped-Si, Ge, Diamond and dimond like carbon	Microelectronic devices	[SiH <sub>4</sub> ], [Si <sub>2</sub> H <sub>6</sub> ] [SiH <sub>4</sub> ] [GeH <sub>4</sub> ] [C <sub>n</sub> H <sub>2n+2</sub> ]
III-V Compound Semiconductors	GaAs	Solar cells, LEDs	Gp.IIItrialkyls,[R <sub>3</sub> M](M=Ga,In,Al& R=Me,Et)
Metal Nitrides	WN	Diffusion Barriers, Gate electrodes in microelectronic devices	[NbCl <sub>5</sub> ]/[NH <sub>3</sub> ]: NbCl <sub>5</sub> ]/[Me <sub>2</sub> NNH <sub>2</sub> ]:[WCl <sub>6</sub> ]/[NH <sub>3</sub> ]: [WF <sub>6</sub> ]/[NH <sub>3</sub> ]

### Examples of CVD films:

Dielectric materials: SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>

Other materials: W, TiN for semiconductors Al, B, C, Co, Fe, Mo, Ni, Nb, Ta

### Advantages:

1. Uniform distribution over large area.
2. Multi directional deposition technique.
3. Conformal deposition
4. No compositional gradients across substrate.
5. No need to break vacuum for source change.
6. More selective area deposition because of higher activation energy for reaction with foreign substances.

### Disadvantages:

1. They are generally not suitable for mixture of material.
2. They are not suitable for material causing chemical reaction.
3. It involves more safety and contamination.
4. High cost for compounds with sufficient purity.

### Applications of CVD technique:



1. Microelectronics: Conductors, Passivation layers, diffusion barriers, oxide barriers etc
2. Semiconductors: Laser of GaAs(Ga,Al)As and InP(In,Ga)As
3. Optical: Optical fibers for telecommunication, It is produced by coating the inside of fiber by fused silicatube with oxide of silicon, germanium, boron etc
4. Solar energy conversion: Thin film solar cells of silicon and gallium arsenide.
5. Carbon nanotubes for advanced electronics, biological and chemical devices and detectors.
6. Wear resistant coatings: Coating of TiC, TiN and Al<sub>2</sub>O<sub>3</sub> on cemented carbide cutting tools (punches, nozzles, free wheels, etc)
7. Corrosion resistant coatings: Ta, Nb, Cr etc
8. Erosion resistant coatings: TiC, Cr<sub>7</sub>C<sub>3</sub>, B<sub>4</sub>C etc
9. Heat resistant coatings: Al<sub>2</sub>O<sub>3</sub>, SiC, Si<sub>3</sub>N<sub>4</sub> etc
10. Superconductors: for medical, power grids, high energy physics etc
11. Fiber for Fiber Reinforced materials ( fiber of boron, SiC, Boron Carbide etc
12. Structural shapes: Tubes, crucible heating elements shapes for Tungsten
13. Decorative coatings: TiN (gold colour) on watches, jewellery etc.
14. Conducting coatings: IC interconnects, display applications, solar control, electrochromic windows, automotive windows

Micro fabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial. These materials include: silicon (SiO<sub>2</sub>, germanium, carbide, nitride, oxynitride), carbon (fiber, nanofibers, nanotubes, diamond and graphene), fluorocarbons, filaments, tungsten, titanium nitride and various high-k dielectrics.

#### Comparison/ difference between PVD and CVD

PVD	CVD
Highly directional deposition	Multidirectional deposition
Non conformal deposition	conformal deposition
Uses physical process only	First physical then chemical process
Uses pure source material	Uses mixed source material
Depositing material used in solid or liquid form at the beginning	Depositing material used in gaseous form always
Deposited at relatively low temp. 250 to 450 °C	Deposited at relatively high temp. 450 to 1050 °C
Deposition occur by condensation	Deposition occur by chemical reaction
Generally no hazardous by product	Hazardous by product
Evaporation is limited to certain materials, sputtering yield problem	Preferred for poly silicon layer and silicon nitride

## Thin Film Applications

In considering the different applications of deposited thin films, the following generic categories can be identified.

**A) Electronic components:** The fabrication of electronic components, especially solid state devices and microelectronics integrated circuits, have undoubtedly found the widest and most demanding applications for thin film depositions. These films typically consist of semiconductors materials, dielectric materials and insulating materials and metals or refractory metal silicon conductors.

**B) Electronic Display:** Electronic display are used for interacting electronic equipments with human operators. Different components and device structures are required such as:

**Liquid-Crystal Displays, Light Emitting Diodes (LEDs), Electroluminescent Displays, Plasma and Fluorescent Displays, Electro chromic Displays**

The fabrication of these displays requires conducting films, transparent and conducting films, luminescent or fluorescent films as well as dielectric and insulating layers.

**C) Optical Coatings:** Optical coatings are applicable for antireflection purpose, as interference filters on solar panels, as plate glass infrared solar reflectors and for laser optics. In fabrication of filter optics, thin films with refractive index gradients are deposited on preforms from which the optical fibers are drawn. These coatings require dielectric materials with precisely defined indices of refraction and absorption coefficients. Laser optics require metal reflective coatings which can withstand high radiation intensities without degradation. Infrared reflecting coatings are applied to filament lamps to increase the luminous flux intensity.

**D) Magnetic films for Data Storage:** Thin films of magnetic materials have found wide commercial applications for data storage in computer and control systems. The substrates can be metal, glass or plastic polymer materials. Thin film deposition processes for magnetic material and for materials with a high degree of hardness are required.

**E) Optical Data Storage Devices:** Thin films are finding increasing commercial use for optical data storage devices in computer disk and computer memory applications. Processes for the deposition of organic polymer materials as storage media and as protective overcoats are required for this technology.

**F) Antistatic Coatings:** Thin films of conductive or semi conductive materials are deposited to provide protection from electrostatic discharges.

**G) Hard Surface Coatings:** Thin film coatings of Carbides, silicides, Nitrides and Borides are finding increased use to improve the wear characteristic of metal surface for tools, bearings and machine parts. Of particularly great current interest are films of diamond like carbon because of this materials heat dissipation properties, electrical insulation, hardness and resistance to high temperature and high energy radiation.

**(Ferroelectric:** All ferroelectric materials are pyroelectric, however, not all pyroelectric materials are ferroelectric. Below a transition temperature called the Curie temperature ferroelectric and pyroelectric materials are polar and possess a spontaneous polarization or electric dipole moment. However, this polarity can be reoriented or reversed fully or in part through the application of an electric field with ferroelectric materials. Complete reversal of the spontaneous polarization is called "switching".

**Applications for Ferroelectric Materials :** Capacitors, Non-volatile memory, Piezoelectrics for ultrasound imaging and actuators, Electro-optic materials for data storage applications, Thermistors, Switches known as transchargers or transpolarizers, Oscillators and filters

- **Ferrites:** Ferrites have importance in engineering and technology because they possess spontaneous magnetic moment below the Curie temperature just as iron, cobalt, nickel.
- Due to very low eddy current losses, ferrites are used as a core of coils in microwave frequency devices and computer memory core elements.
- Due to relatively low permeability and flux density compared to iron, ferrites are not suitable for the use in high field and high power applications, such as motors, generators and power transformers, but they can be used in low field and low power applications.
- Ferrites are used as ferromagnetic insulators in electrical circuits.
- Ferrites like ZnO find low frequency applications in timers. They are also used as switches in refrigerators, air conditioners, etc.
- Ferrites are used as magnetic head transducer in recording.

**Dielectric Oxides:** Very thin films are generally impractical for microelectronic applications because of their nonuniformity and the high density of pin holes. Thick films are generally used for resistors (and capacitors) but their properties are not very precisely controlled. Thin films, on the other hand, are used in a variety of applications in the technology of microelectronics. They may be conductive, resistive, or insulating and their characteristics are not always the same as those of the bulk material. We shall restrict ourselves here to thin dielectric films.)