

## **Thin films**

A thin film in general, refers to films with thickness ranging from 0.1  $\mu\text{m}$  to about 300  $\mu\text{m}$ . Coatings such as paint or varnish are typically much thicker. Thin film coatings have unique properties and hence make them desirable for a variety of reasons including materials conservation and design flexibility. A large number of materials which are used for coatings today range from the naturally occurring oxide layer (which protects the surfaces of many metals such as aluminum, titanium, and stainless steel), to those with very deliberate and controlled alloying additions to the surface to produce specific properties as follows;

- Chemically stable in the environment where it is used
- Adhere well to the substrate
- Uniform thickness
- Chemically pure or of controlled chemical composition
- The low density of imperfections
- Optical or magnetic properties, insulator or semiconductor as required for particular applications

As the film is inherently fragile, the bonding between the thin film and substrate provides the structural support. The bonding forces may be primary chemical in nature. Eg. The oxide lattices of the metal oxide and the glass blend at the interface forming a thin zone of intermediate composition. The bonding energies are in the range of 250 - 400 kJ/mol. In some cases, the bonds are based on intermolecular van der Waals and electrostatic forces. The energies are in the range of 50-100 kJ/mol. Eg. Deposition of polymer film on a metal surface

## **Uses of thin films**

They are used as conductors, resistors and capacitors. They are widely used as optical coatings on lenses to reduce reflection and to protect the softer glass against scratching. Thin metallic films have been used as protective coatings on metals. Eg. Silver plating, chrome plating. Metal tool surfaces are coated with ceramic thin films to increase their hardness. The top of the drill bit is normally coated with a thin film of tungsten carbide to impart hardness and wear resistance. The films are applied to the glass to reduce scratching and abrasion and to increase lubricity.

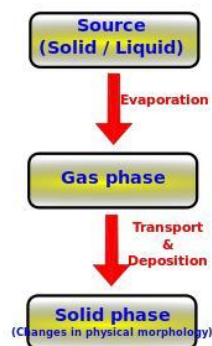
## Formation of thin films

The process of applying a thin film to a surface is known as thin-film deposition or fabrication. It is the technique for depositing a thin film of material onto a substrate or onto previously deposited layers. Thin films are formed by different techniques such as physical vapor deposition (PVD) or chemical vapor deposition (CVD). In PVD there is no change in the chemical nature of the source and coated material whereas in CVD due to chemical reactions occurring, the chemical identity of the source and the coated thin film materials are different.

### Physical vapor deposition

PVD processes are atomistic deposition processes in which material is vaporized to form a solid or liquid source in the form of atoms or molecules, transported as vapor through a vacuum or low pressure gaseous (or plasma) environment to the substrate where it condenses. The material to be deposited is placed in an energetic, entropic environment so that particles of material escape its surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particles to travel as freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal.

Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers to thousands of nanometers. The substrates can range in size from very small to very large, in shape from flat to complex geometries. The source-substrate geometry influences the ultimate film uniformity. Two principal methods for optimizing film uniformity over large areas involve varying the geometric location of the source and interposing static as well as rotating shutters between evaporation sources and substrates. The chemical purity of evaporated films depends on the nature and level of impurities that (1) are initially present in the source, (2) contaminate the source from the heater, crucible, or support materials, and (3) originate from the residual gases present in the vacuum system. Typical PVD deposition rates are 10-100 Å/s.



**Fig. PVD: Process flow diagram**

Vacuum evaporation is one of the important methods for depositing thin films using PVD technique.

**Vacuum deposition:** This method is used to form thin films of substances that can be vaporized without destroying their chemical identities. Eg. Optical lenses are coated with inorganic materials such as  $\text{MgF}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . During evaporation, a target consisting of the material to be deposited is bombarded by a high energy source such as a beam of electrons or ions in a high vacuum chamber with a pressure of  $10^{-5}$  torr or less. This dislodges atoms from the surface of the target, 'vaporizing' them. Vaporized atoms from the target move in a straight path to the substrate to be coated. Finally, the metal atoms get deposited on the substrate surface mounted at an appreciable distance away from the evaporation source. Uniformity is obtained by rotating the substrate to be coated.

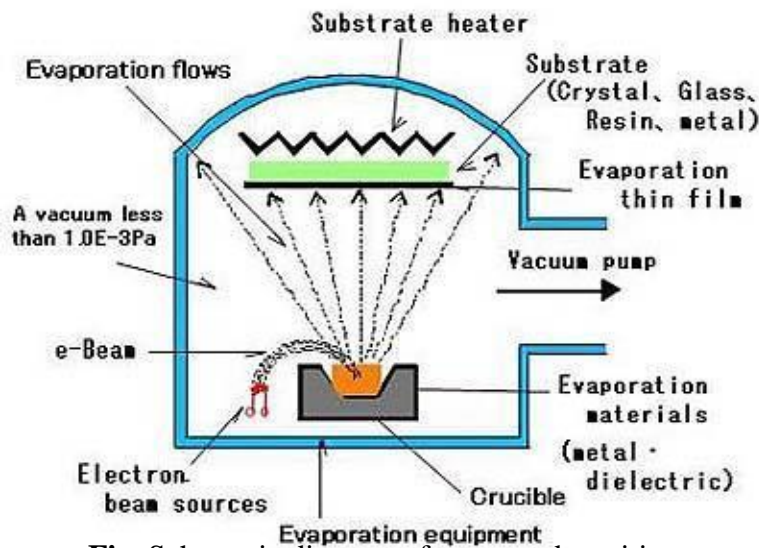


Fig. Schematic diagram of vacuum deposition

The vacuum environment may serve the following purposes by providing low pressure plasma environment, a means for controlling gas and vapor composition and a means for mass flow control into the processing chamber. And reducing the particle density of undesirable atoms and molecules (contaminants) so that the mean free path for collision is long

**Advantages:**

- PVD coatings are harder and more corrosion resistant than coatings applied by the electroplating process.
- Most coatings have high temperature and good impact strength, excellent abrasion resistance

- More environmentally friendly than traditional coating processes such as electroplating and painting.
- It is possible to change the target material without disturbing the system so that multilayer films can be formed.

***Disadvantages:***

- It is extremely difficult to coat undercuts and similar surface features
- High capital cost
- Some processes operate at high vacuums and temperatures, require skilled operators
- Processes involving a large amount of heat requires appropriate cooling systems
- The rate of coating deposition is usually quite slow

**Chemical Vapor Deposition (CVD)**

In this method, the surface is coated with a volatile, stable chemical compound at a temperature below the melting point of the surface. It involves the dissociation and /or chemical reactions of gaseous reactants in an activated (heat, light, plasma) environment, followed by the formation of a stable solid product. The deposition involves homogenous gas phase reactions, which occur in the gas phase, and/or heterogeneous chemical reactions which occur on/near the vicinity of a heated substrate leading to the formation of powders or films, respectively. It has been used to produce ultrafine powders and thin films.

In general, the CVD equipment consists of three main components:

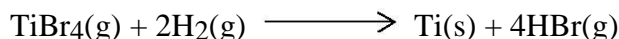
- (a) Chemical vapor precursor supply system: to generate vapor and deliver to the reactor.
- (b) CVD reactor component: consists of a reaction chamber equipped with a load-lock for the transport and placement of the substrate into the chamber, a substrate holder, and a heating system with temperature control. The main function is to heat the substrate to the deposition temperature.
- (c) Effluent gas handling system: This component consists of a neutralizing part for the downstream gases, and /or a vacuum system to provide the required reduced pressure for the CVD process.

***Process principles and deposition mechanism:*** CVD process involves the following key steps:

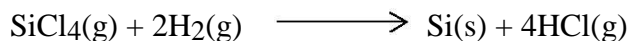
1. Generation of active gaseous reactant species

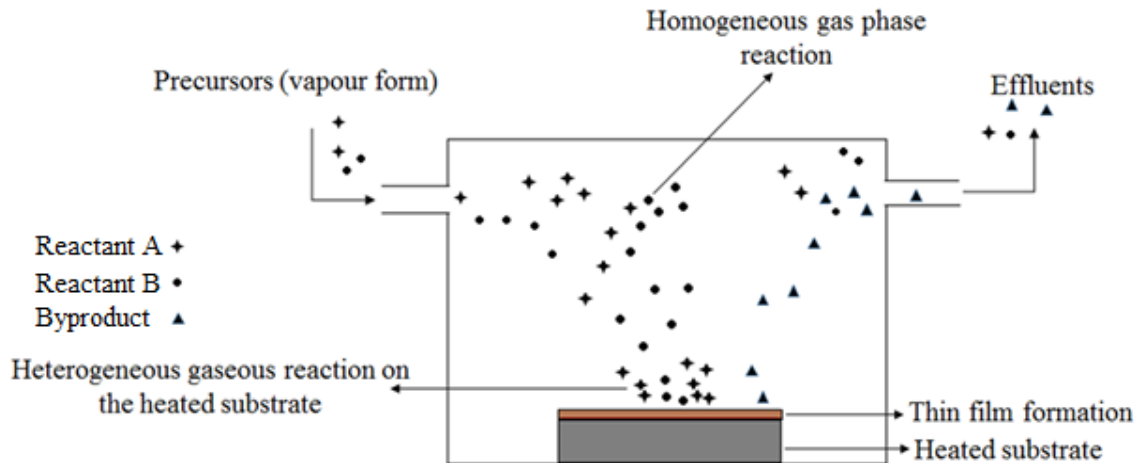
2. Transport of these gaseous species into the reaction chamber.
3. Gaseous reactants undergo gas phase reactions forming intermediate species.
  - (a) At a high temperature above the decomposition temperatures of intermediate species inside the reactor, homogeneous gas phase reaction can occur where the intermediate species undergo subsequent decomposition and/or chemical reaction.
  - (b) At temperatures below the dissociation of the intermediate phase, diffusion/convection of the intermediate species across the heated substrate surface occur. These intermediate species subsequently undergo steps (4-7)
4. Adsorption of gaseous reactants on to the heated substrate and the heterogeneous reaction occurs at the gas-solid interface (i.e. heated substrate) which produces the deposit and by-product species.
5. The deposits will diffuse along the heated substrate surface forming the crystallization center and growth of the film takes place.
6. Gaseous by-products are removed from the boundary layer through diffusion or convection.
7. The unreacted gaseous precursors and by-products will be transported away from the deposition chamber.

Examples: Titanium tetrabromide is evaporated and the gaseous  $\text{TiBr}_4$  is mixed with hydrogen. The mixture is then passed over a substrate heated to about  $1300^\circ\text{C}$ , such as silica or alumina. The metal halide undergoes reaction with hydrogen to form a thin film of titanium metal



Films of silicon are formed by decomposing  $\text{SiCl}_4$  in the presence of  $\text{H}_2$  at  $1200^\circ\text{C}$ .





**Fig.** Schematic diagram of simplified CVD reactor

### *Advantages*

- Capable of producing highly dense and pure materials without carbon or oxygen impurities.
- Produces uniform films with good reproducibility and adhesion at reasonably high deposition rates.
- Has good throwing power and hence can be used to uniformly coat complex shaped components and deposit films.
- Able to control crystal structure, surface morphology and orientation of the products by controlling the process parameters.
- Deposition rate can be adjusted readily. The low deposition rate is favored for the growth of epitaxial thin films for microelectronic applications. The deposition of thick protective coatings is favored by a high deposition rate.
- Reasonable processing cost using the CVD technique.
- The flexibility of using a wide range of chemical precursors such as nitrides, borides, organometallics which enable the deposition of a large spectrum of materials including metal carbides, nitrides, oxides and sulfides.

### *Drawbacks*

- Chemical and safety hazards caused by the use of toxic, corrosive, flammable and/or

explosive precursor gases.

- Difficult to deposit multicomponent materials with well-controlled stoichiometry using multisource precursors because different precursors have different vaporization rates.
- The use of more sophisticated reactor and /or vacuum system by CVD variants such as low pressure or ultrahigh vacuum CVD, plasma-assisted CVD and photo-assisted CVD tends to increase the cost of fabrication.

#### ***Applications:***

- Production of high-quality optical fibers suitable for long distance applications.
- Diamond thin films: They are used as heat sinks for microelectronics and optoelectronics, sensors, microwave devices, coatings for IR windows in nuclear detectors, UV imaging, cold cathodes. The potential applications of diamond films involve speaker diaphragms which are coated with thin films of diamond to provide improved acoustic properties.

#### **Comparison between PVD & CVD**

<b>Features</b>	<b>PVD</b>	<b>CVD</b>
Mechanism of deposition	Thermal energy	Chemical reaction
Deposition rate	High	Moderate
Deposited species	Atoms & ions	Precursor molecules dissociate into atoms
Energy of deposited species	Low (0.1-0.5 eV)	Low; can be high with plasma-assisted CVD
Throwing power	Poor	Good

#### **Nano-materials**

Nanoscience and nanotechnology deal with objects that have dimensions in the range from 1

nm to about 100 nm. Nano-materials are materials which have at least one of their dimension in the nanometer ( $1\text{ nm} = 10^{-9}\text{ m}$ ) range. The physical and chemical properties of nano-materials differ significantly from those of their bulk counterparts. The new properties are the result of an increase in the ratio of surface area to volume. This will change the surface effects such as those that give rise to catalysis, adsorption, adhesion and photonic effects. The reason for this is that the electrons in nanomaterials are confined within such a small volume that quantum effects now dominate optical and electronic behavior. Nano-fibers, nano-wires, nano-scale particles, Nano-channels and nano-tubes are some of the important nanostructures. The nano-science field is progressing so rapidly that it is probably hard to find any technical areas that are not useful.

The most important aspects of this field are connected with four issues;

- i) The way in which nanoparticles interact with their neighbors in solid arrays or with the second phase in composite materials.
- ii) Miniaturization of electronic circuits below the micro-scale to pack an increasing number of features into an integrated array.
- iii) Development of methods to produce nano-fibers that are of interest in geological tissue engineering, advanced textiles and filtration technology.
- iv) Use of micelles with diameters in the nano range for controlled drug delivery.

## **Classification**

### **(a) Based on origin**

*(i) Natural nanomaterials*

*(ii) Artificial nanomaterials*

Natural nanomaterials are those which are obtained naturally. Examples:- Carbon-nanotubes and fibers. Artificial nanomaterials are those which are synthesized artificially Examples:- Au/Ag nanoparticles, Polymeric nano-composites.

### **(b) Based on dimension**

This classification is based on the number of dimensions which are not confined to the nanoscale range ( $<100\text{nm}$ ). They may be amorphous or crystalline, single crystalline or polycrystalline, made up of one or more elements, metallic, ceramics or polymers.



(i) *Zero-dimensional*: Materials wherein all the dimensions are within the nanoscale range are called zero-dimensional nanomaterial. Eg: quantum dots.

(ii) *1 dimensional*: Here two dimensions are at the nanoscale range, another dimension is not. This leads to needle-like nanomaterials. Eg: nanotubes, nanorods, nanowires.

(iii) *2 dimensional*: Here one dimension is at the nanoscale range, the other two dimensions are not. They exhibit plate-like shapes. Eg: nanocoatings, nanofilms

(iv) *3 dimensional*: These materials are not confined to the nanoscale in any dimension. These are characterized by having three arbitrarily dimensions above 100 nm. They are also known as bulk nanomaterials. 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nano wires/nanotubes as well as multilayers. Eg: Nanocrystalline materials, nanospheres.

There are other types of classifications based on their field of application, shapes, properties, structures, manufacturing process and morphologies.

### **Preparation of nanomaterials:**

Nanomaterials can be synthesized by two different approaches. They are “Bottom-up” and “Top-down methods”. Top-down methods start with micro – or macro scale materials, which are then broken down chemically or physically to nanoparticles. Methods that are used include ball milling, chemical etching, electrospinning and the vaporization of metals using plasmas. They are slow, not cheap, and not suitable for large-scale production. Bottom-up methods involve the assembly of very small units (atoms, molecules or small nanoparticles) to create larger nanomaterials and systems. The fabrication is much less expensive.

### **“Bottom-up” Approach:**

#### **Sol-gel method**

The sol-gel process is a wet-chemical technique used primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for the preparation of gel by either discrete particles or network polymers. The process usually consists of five steps:

1. *Preparation of a precursor solution*: The desired colloidal particles are dispersed in a liquid to form a sol. Typical precursors are metal alkoxides, which undergo various forms of hydrolysis and polycondensation reactions. The formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.

2. Deposition of the sol onto a substrate: The sol solution is coated on a substrate by spraying, dipping or spinning.
3. Formation of gel: The particles in the solid state are polymerized through the removal of the stabilizing components. This can be done either by heating the sol at a low temperature or allowing it to stand for a certain duration. This results in the formation of a gel.
4. Drying process: Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification.
5. Heat Treatment: After drying, a thermal treatment, or firing process, is often necessary to favor further poly-condensation reaction and enhance mechanical properties, structural stability of the gel.

The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used as a means of producing very thin films of metal oxides for various purposes. Examples include Gallium based nano-materials, Dye-doped gel Glasses, Glass dispersed liquid crystals, Synthesis of glass-metal nano-composite, Metal-silica and Metal oxide-silica nanocomposites.

### **“Top Down” Approach:**

#### **Ball Milling**

In this process, small balls are allowed to rotate around the inside of a drum and drop with gravity force on to a solid enclosed in the drum. The significant advantage of this method is that it can be readily implemented commercially. The grinding of ceramics can reduce them to a fine powder with each individual particle having nanoscale dimensions. It is difficult to avoid contamination of the nanoparticles by the materials used in the abrasion process and the particle sizes are not uniform. Polymers cannot be reduced to nanoparticles by grinding because of their molecular structure and their impact resistance. Ball milling can be used to make a variety of new carbon types, including carbon nanotubes. It is useful for preparing other types of nanotubes, such as boron nitride nanotubes and a wide range of elemental and oxide powders. For example, iron with grain sizes of 13-30 nm can be formed. Ball milling is the preferred method for preparing metal oxides.

To successfully prepare metal oxides, it is important to keep the crystallites from reacting and to

have an understanding of the kinetic energy transferred during crushing. However, a by-product can sometimes be useful. In the production of nanocrystalline Zirconia ( $\text{ZrO}_2$ ), zirconium chloride is treated with magnesium oxide during milling to form zirconia and magnesium chloride:



The by-product, magnesium chloride, acts to prevent the individual nanocrystallites of zirconia agglomerating. It is washed out at the end of the process.