

THIN FILMS

Films with thickness ranging from 0.1- 300 μm .

Thin film coating produces specific surface properties such as

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

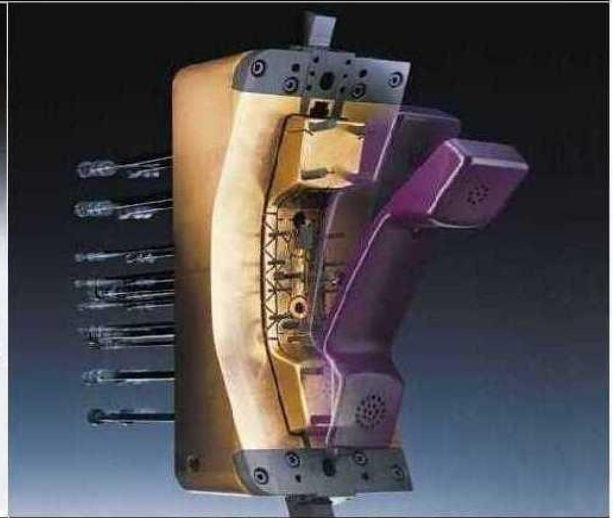
PVD thin film coatings, offering tailor made solutions for:



Metal Cutting



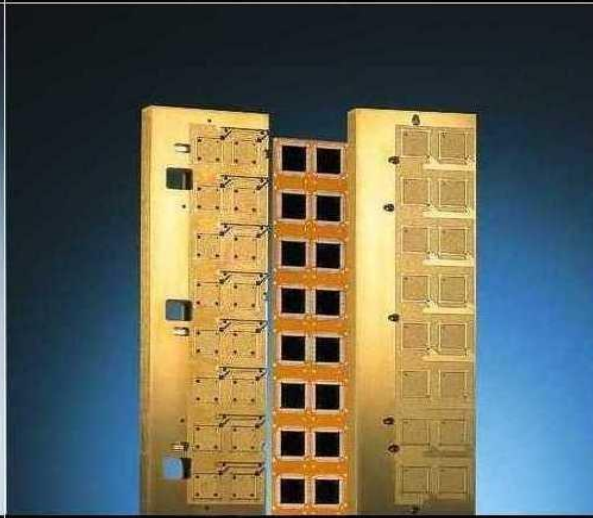
Stamping / Forming



**Plastic Injection
Molding**



CD / DVD Moulding



IC Encapsulation



**Precision
Components**



OCCHIALERIA
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OROLOGERIA

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KEY-COMPONENTS

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TAPS

AUTOMOTIVE

FLATWARE
POSATERIA

Bonding between thin film and substrate

Bonding forces may be

1) Primary chemical in nature.

- Bond energies in the range of 250 to 400 kJ/mol.
- Example - The oxide lattices of the metal oxide on to the substrate.

2) Van der Waals and electrostatic forces.

- Bond energies in the range of 50-100 kJ/mol.
- Example - Deposition of organic polymer film on a metal surface.

Uses

- As conductors, resistors & capacitors
- As optical coatings on lenses to reduce reflection & to protect the softer glass against scratches.
- As protective coatings on metals. Eg. Silver plating, chrome plating.
- Ceramic film coating on metal surfaces to increase hardness Eg. Tungsten carbide film on drills.

Formation of thin films

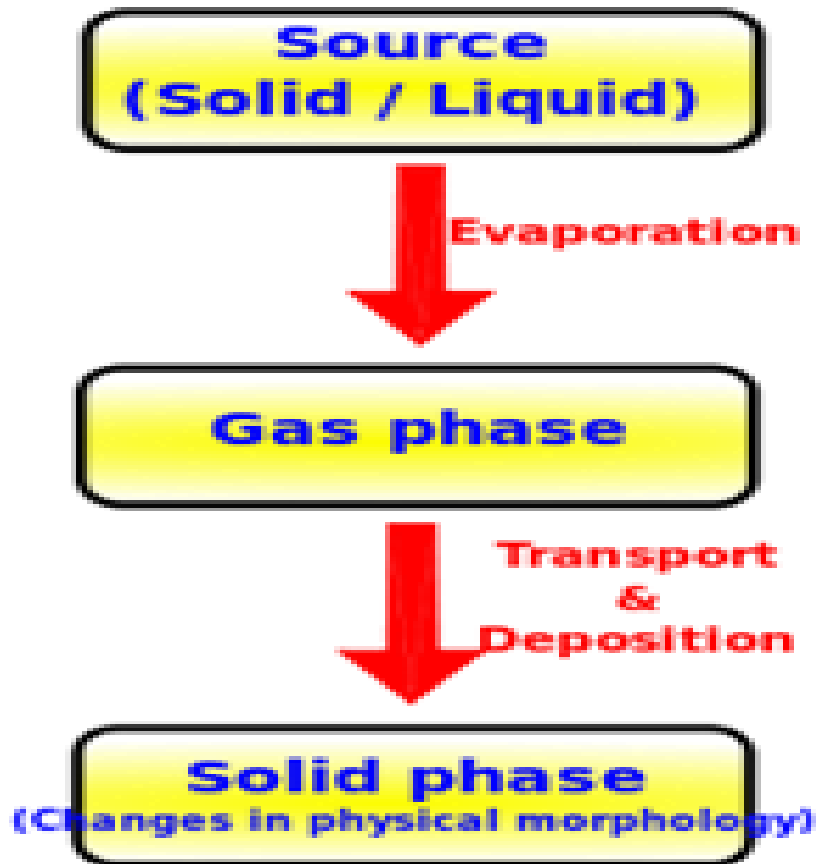
The process of applying a thin film to a surface is known as thin-film deposition or fabrication.

Different techniques of thin film formation

- i) Physical vapor deposition (PVD)
- ii) Chemical vapor deposition (CVD)

When the vapor source is a liquid or solid, the process is called **physical vapor deposition (PVD)**. When the vapor source is a chemical vapor precursor the process is called **chemical vapor deposition (CVD)**.

Physical Vapor Deposition (PVD)



PVD processes are atomistic deposition processes in which material is vaporized **from 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.

Physical Vapour Deposition is done in two methods – i) Vacuum evaporation/deposition, ii) Sputtering

The chemical purity of evaporated films depends on the nature and level of impurities that

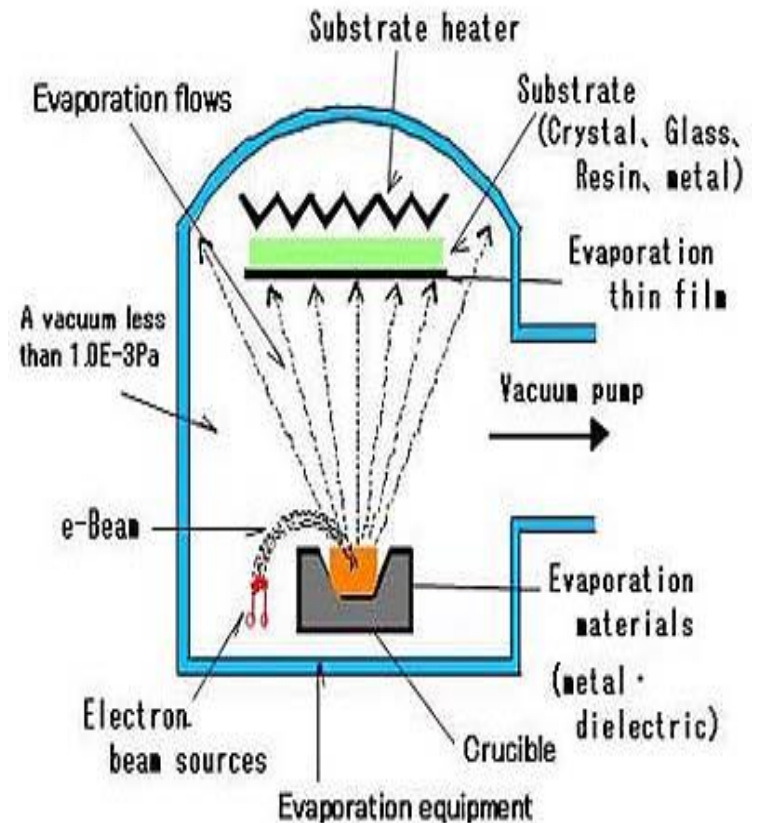
- (1) are initially present in the source
- (2) contaminate the source from the heater, crucible, or support materials
- (3) originate from the residual gases present in the vacuum system

Vacuum deposition

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

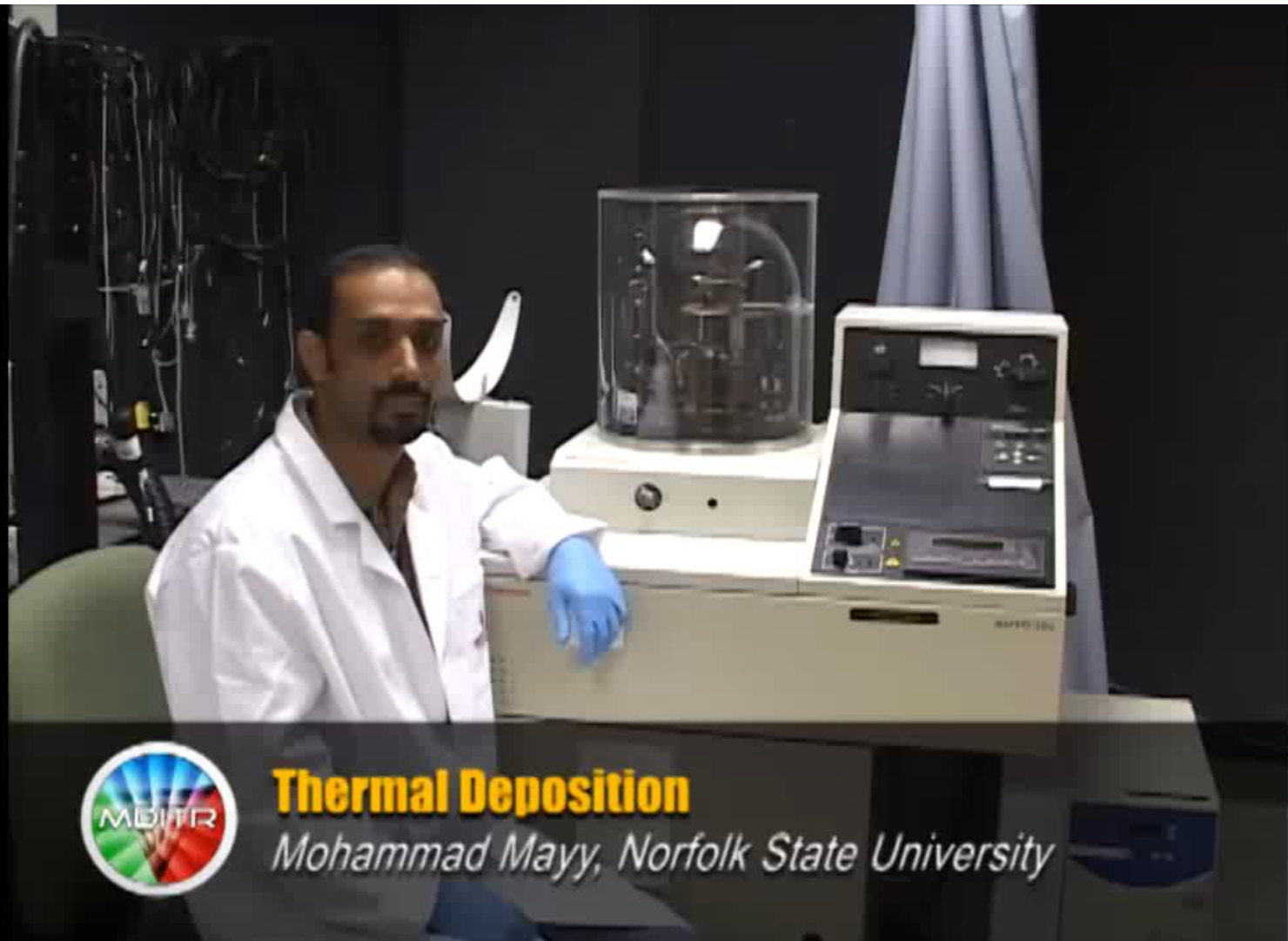
This method is used to form thin films of substances that can be vaporized without destroying their chemical identities.

Example: Optical lenses are coated with inorganic materials such as MgF_2 , Al_2O_3 and SiO_2 .



The vacuum environment may serve the purposes such as -

- i) Providing low pressure plasma environment, a means for controlling gas and vapour composition.
- ii) A means for controlled flow of mass (quantity) into the processing chamber.



Thermal Deposition

Mohammad Mayy, Norfolk State University

<https://www.youtube.com/watch?v=f7UxBawRPj4>

Advantages of PVD

- Coatings harder & more corrosion resistant
- Have high temperature & good impact strength, excellent abrasion resistance & durable.
- Able to use several types of inorganic & organic coating materials on diverse group of substrates using a wide variety of finishes.
- Eco-friendly than traditional processes.
- Possible to change the target material without disturbing the system so that multilayer films can be formed.

Disadvantages of PVD:

- Extremely difficult to coat undercuts and similar surface features (\therefore known as line of sight technique).
- High capital cost.
- Some processes operate at high vacuums & temperatures.
- Requires appropriate cooling systems.
- The rate of coating deposition quite slow.

Chemical Vapor Deposition (CVD)

In this method the surface is coated with a 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.

Main components of CVD equipment

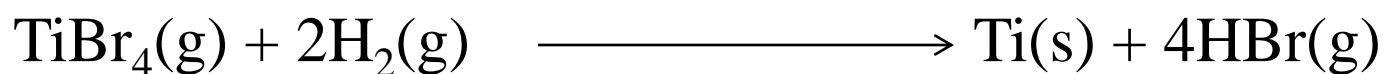
- ✓ Chemical vapor precursor supply system
- ✓ CVD reactor component consisting of load lock, substrate holder and heating system
- ✓ Effluent gas handling system

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

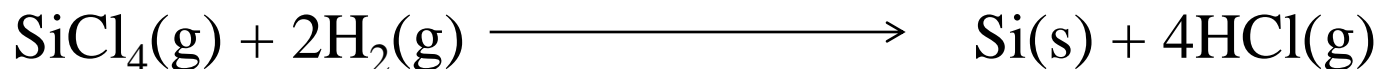
1. Generation of active gaseous reactant species.
2. Transport of these gaseous species into the reaction chamber.
3. In homogeneous gas phase reactions, the intermediate species are formed subsequent decomposition forming powder and volatile by-products.
4. Adsorption of gaseous reactants on to the heated substrate, and the heterogeneous reaction occurs at the gas-solid interface (i.e. heated surface) 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
7. The unreacted gaseous precursors and by-products will be transported away from the deposition chamber.

Examples: Titanium tetrabromide is evaporated and the gaseous TiBr_4 is mixed with hydrogen. The mixture is then passed over a substrate heated to about $1300\text{ }^\circ\text{C}$, such as silica or alumina. The metal halide undergoes reaction with hydrogen to form a thin film of titanium metal on the substrate.



Films of silicon are formed by decomposing SiCl_4 in the presence of H_2 at $1200\text{ }^\circ\text{C}$.



Advantages

- Produces highly dense & pure materials
- Uniform films with good reproducibility & adhesion
- Good throwing power
- Control over crystal structure, surface morphology & orientation of the products
- Deposition rate can be adjusted
- Use a wide range of chemical precursors

Drawbacks

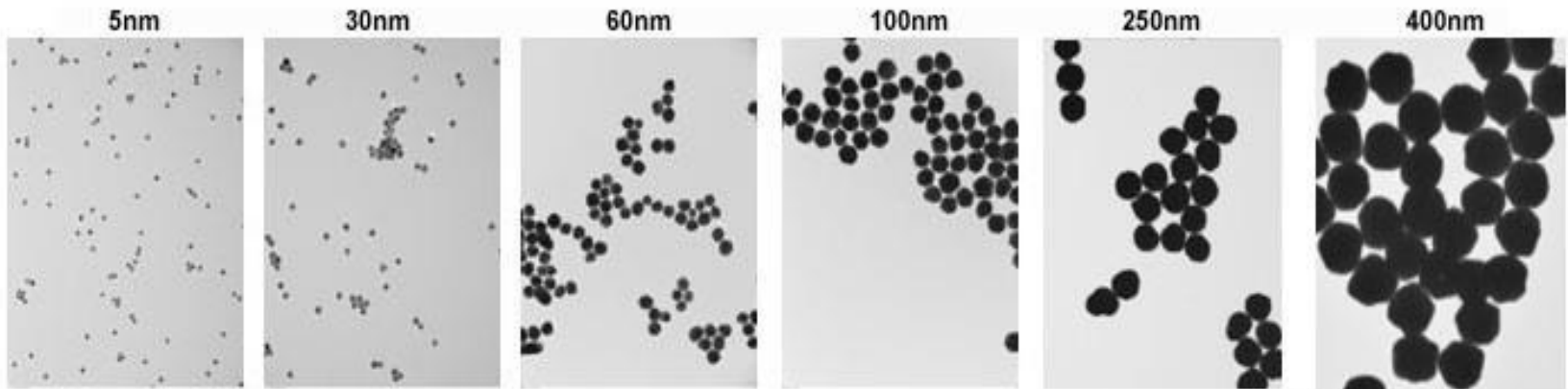
- Chemical & safety hazards caused by the use of toxic $[\text{Ni}(\text{CO})_4]$, corrosive $[\text{SiCl}_4]$, flammable &/or explosive $[\text{B}_2\text{H}_6]$ precursor gases.
- By-products are sometimes hazardous in nature (CO, HF etc.)
- Difficult to deposit multicomponent materials with well controlled stoichiometry using multisource precursors.
- It leads to stress in films deposited on materials with different thermal expansion coefficients, which can cause mechanical instabilities in the deposited films.
- High fabrication cost.

Comparison between PVD & CVD

Features	PVD - Vacuum evaporation	CVD
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

Nanomaterials

- dimensions - 1 to 100 nm
- Large surface area to volume



Classification

Based on

Origin

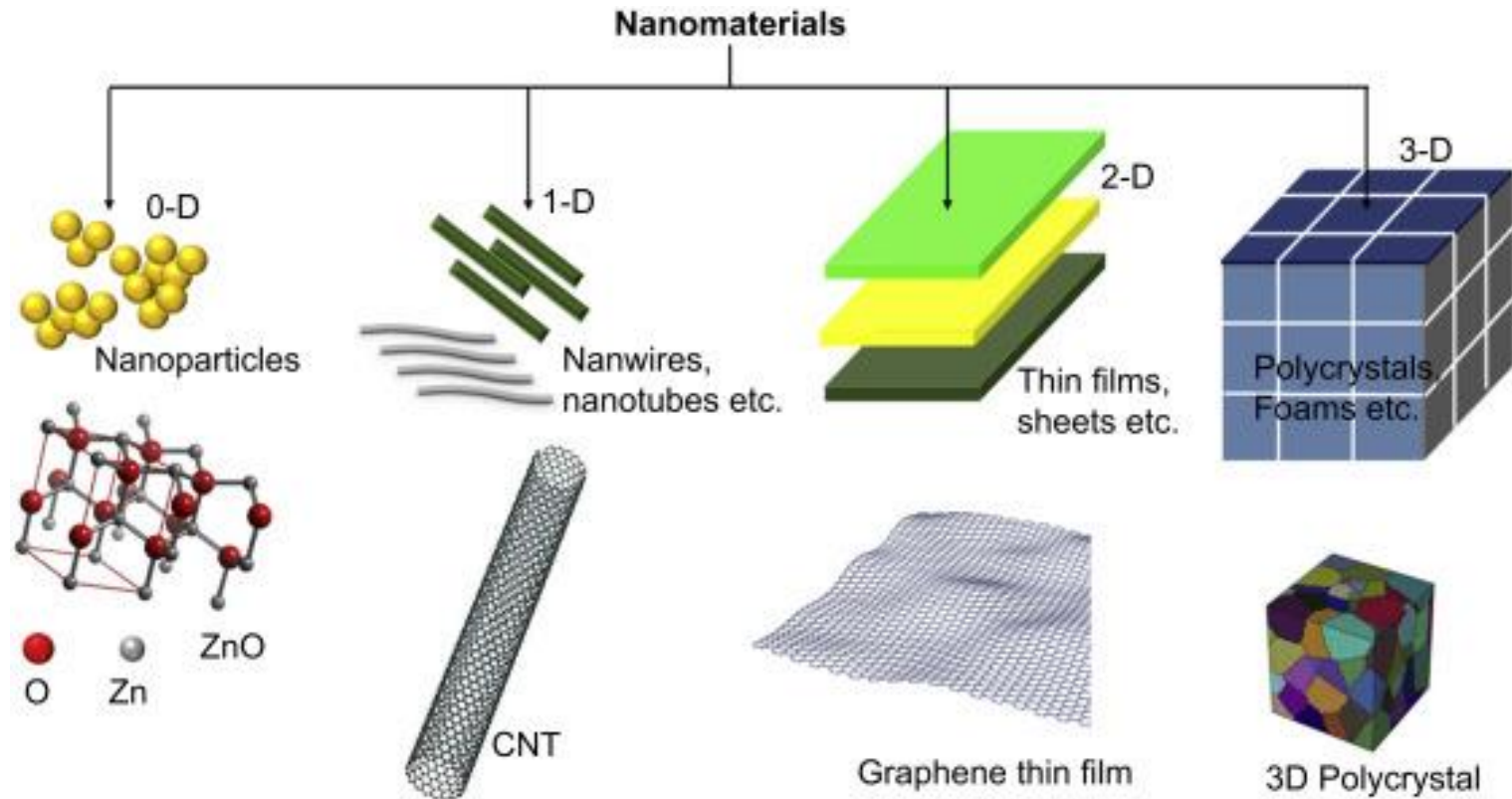
- ✓ Natural - Carbon nanotubes
- ✓ Artificial – Ag/Au nano particles, Polymeric nano composites

Dimension

This classification is based on the number of dimensions which are **not confined to the nanoscale range** (< 100 nm).

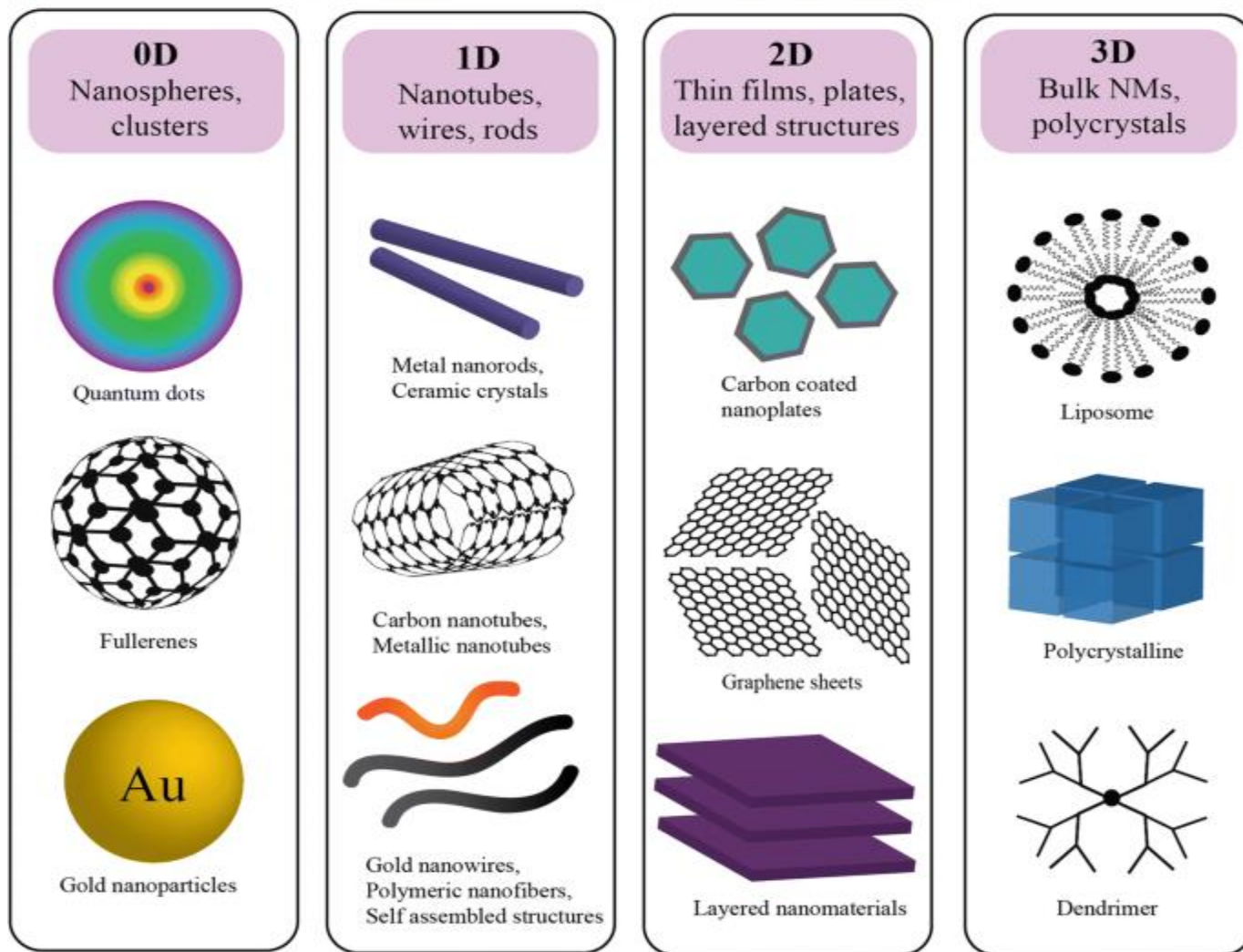
- ✓ Zero dimensional, Eg: quantum dots
- ✓ 1 dimensional, Eg: nanotubes, nanowires
- ✓ 2 dimensional, Eg: nano films
- ✓ 3 dimensional, Eg: nano spheres (Bulk nano materials)

Bulk nano material, contain dispersion of nanoparticles like bundles of nanotubes or nanowires, mainly used in drug delivery systems



Ref: Bansi Dhar Malhotra, Md. Azahar Ali, in [Nanomaterials for Biosensors](#), 2018

NMs classification based on dimensionality



Poh, T.Y., Ali, N.A.B.M., Mac Aogáin, M. *et al.* Inhaled nanomaterials and the respiratory microbiome: clinical, immunological and toxicological perspectives. *Part Fibre Toxicol* **15**, 46 (2018). <https://doi.org/10.1186/s12989-018-0282-0>

Preparation of nano-materials

- **Top down:** Top-down methods start with micro – or macroscale materials, which are then broken down chemically or physically to nanoparticles.
- **Bottom up:** Bottom up methods involve the assembly of very small units (atoms, molecules or small nanoparticles) to create larger nanomaterials and systems.

1) Bottom up:

i) Vapor deposition

- ❖ Physical VD
- ❖ Chemical VD

ii) Chemical synthesis

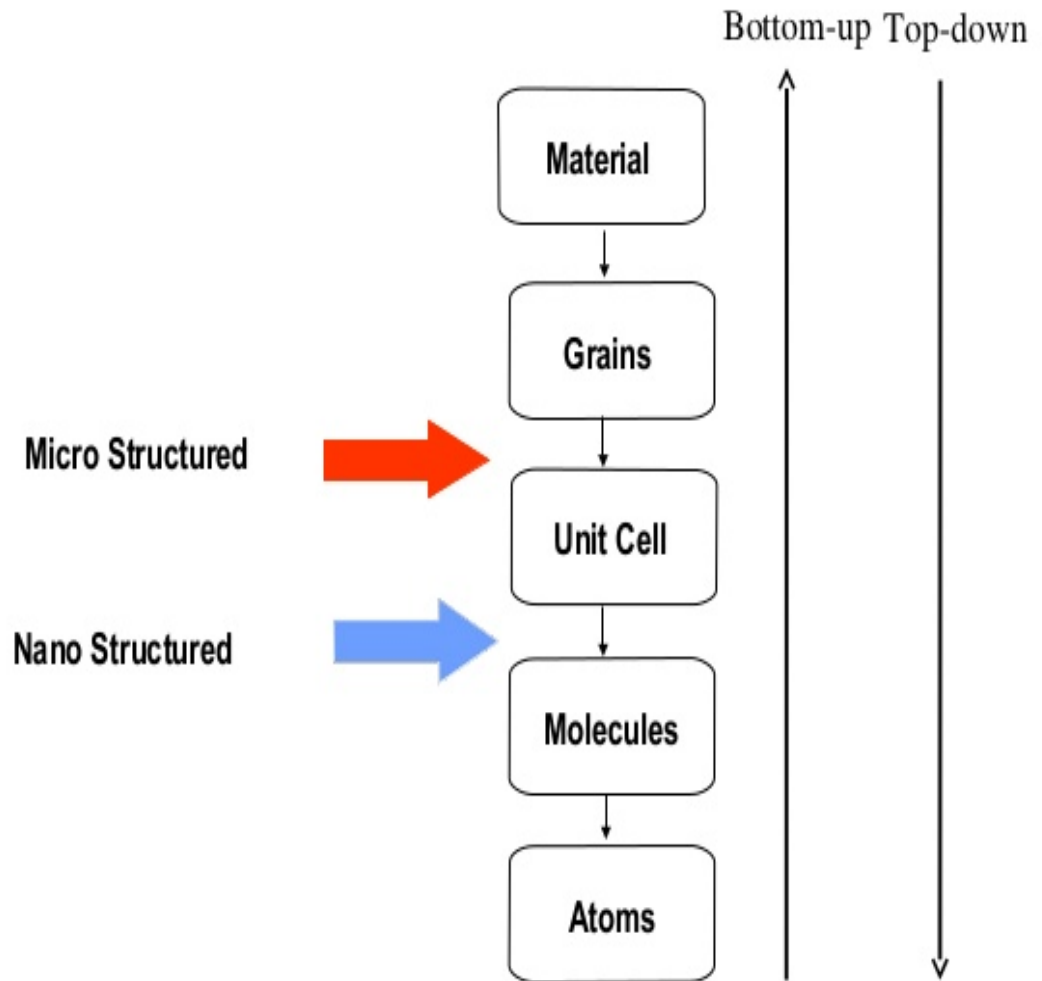
- ❖ Sol gel method
- ❖ Reduction method

iii) Electrodeposition

2) Top-down:

i) Ball milling

ii) Solution combustion method



Chemical Synthesis

a) Sol-gel method

Steps involved

- Preparation of a precursor solution
- Deposition of the sol onto a substrate
- Formation of gel
- Drying process
- Heat Treatment

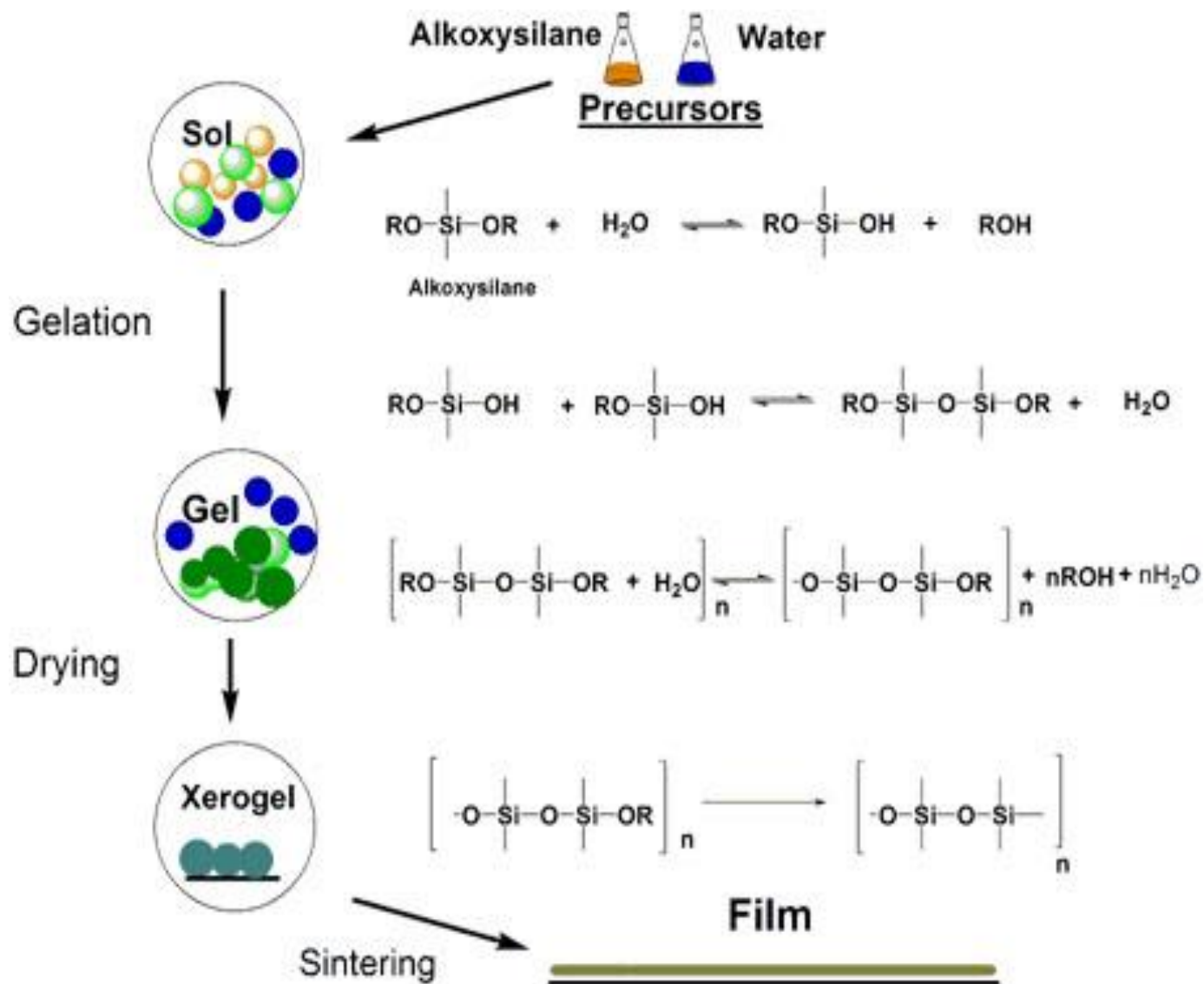
1. *Preparation of a precursor solution*: The desired colloidal particles are dispersed in a liquid to form a sol. Typical precursors are metal alkoxides, which undergo various forms of hydrolysis and polycondensation reactions. The formation of a metal oxide involves connecting the metal centers with 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 polymerised 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 certain duration.

4. *Drying process*: Removal of the remaining liquid phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be evaporated or extracted is ultimately determined by the distribution of porosity in the gel.

5. *Heat Treatment/firing*: After drying, a thermal treatment, or firing process, is often necessary to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth.

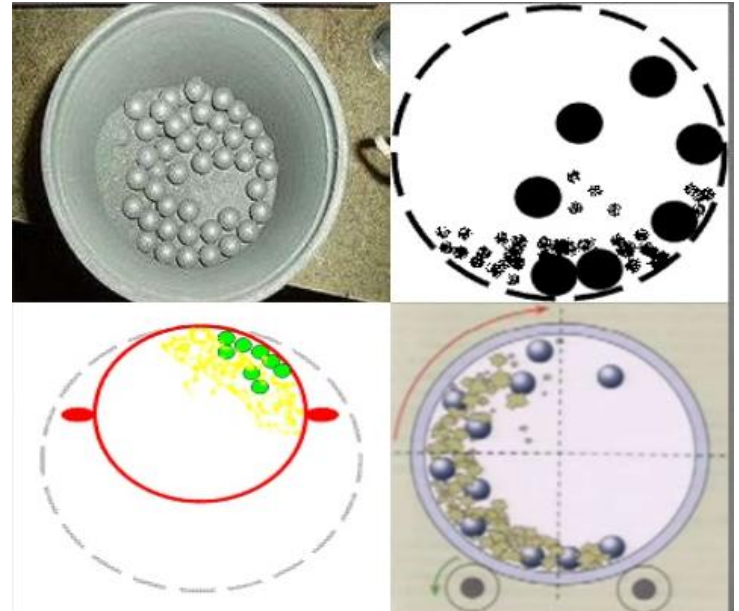


Advantages of Sol-Gel Technique:

- ❖ The sol-gel method is cost effective
- ❖ The process is carried out at low temperature and hence chemical composition of the final compound can be controlled
- ❖ The small quantities of dopants, such as organic dyes and rare earth elements, can also be introduced in the sol to modify the overall properties of the final product.
- ❖ Very thin films of metal oxides can be produced using this method

Ball milling

- In ball milling technique the solid ceramic material which is to be grinded is placed at the bottom of inside drum.
- 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 and hence crush the solid into nanoparticle size



Video Presentation of Ball Milling

<https://www.youtube.com/watch?v=MikiTYpg2aQ>

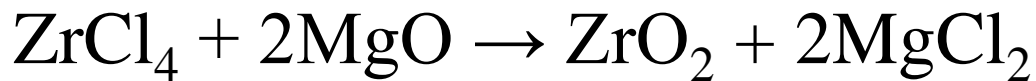
Video Presentation of sophisticated Ball Mill



<https://www.youtube.com/watch?v=5ShOAS3EGGU>

Examples:

In the production of nanocrystalline Zirconia (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.

Disadvantage:

- Polymers cannot be reduced to nanoparticles by grinding because of their molecular structure and their impact resistance.
- It is difficult to avoid contamination of the nanoparticles by the materials used in the abrasion process and the particle sizes are not uniform.