Unit-4
Nano Technology

Introduction:

A nanometre is one billionth of a metre.
For comparison, Size (thickness) of

- a human hair is ~ 80,000nm
- a red blood cell is ~ 7,000nm
- a water molecule is ~ 0.3nm

•Scientists are interested in nanoscale materials with 1nm to 100nm

Properties:

Properties of materials at nanoscale are different from larger scale
Thermodynamics properties are drastically different from nanoparticles
Examples:

•Melting point of gold decreases from 1200K to 800K when the particle size decreases from 300°A to 20 °A.

•In metals if the size is reduced from the bulk the electronic bands become narrower and the value of ionization potential is raised.

Quantum Confinement Effect

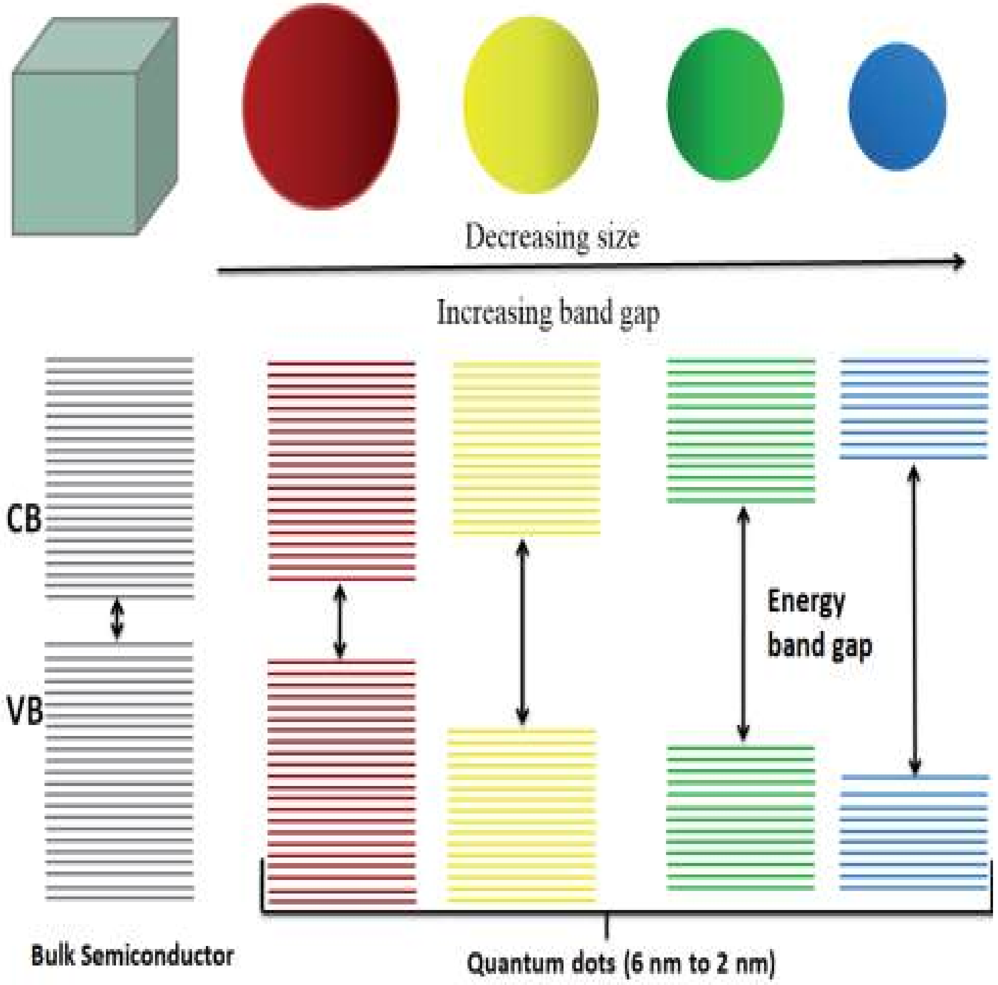
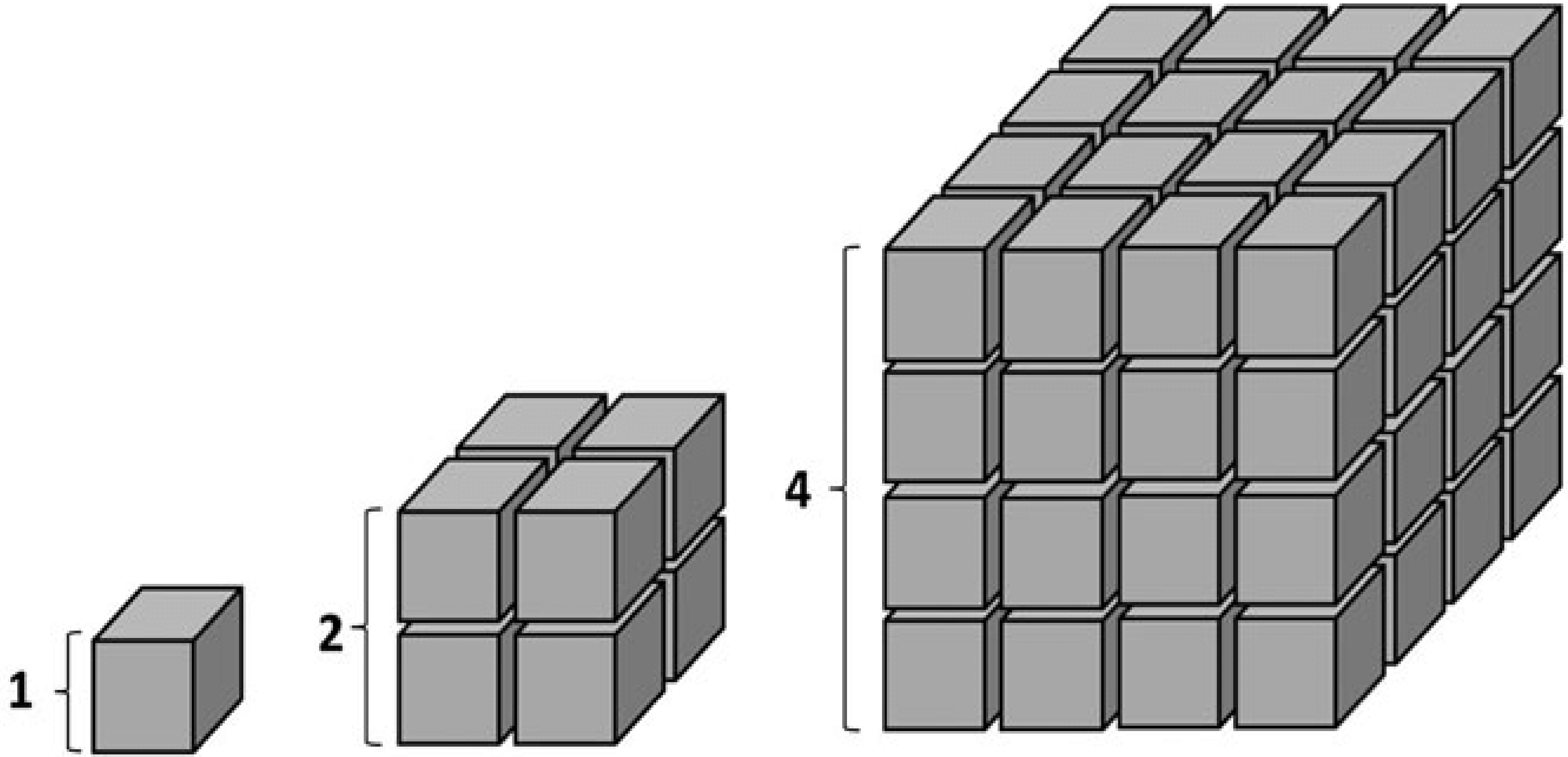


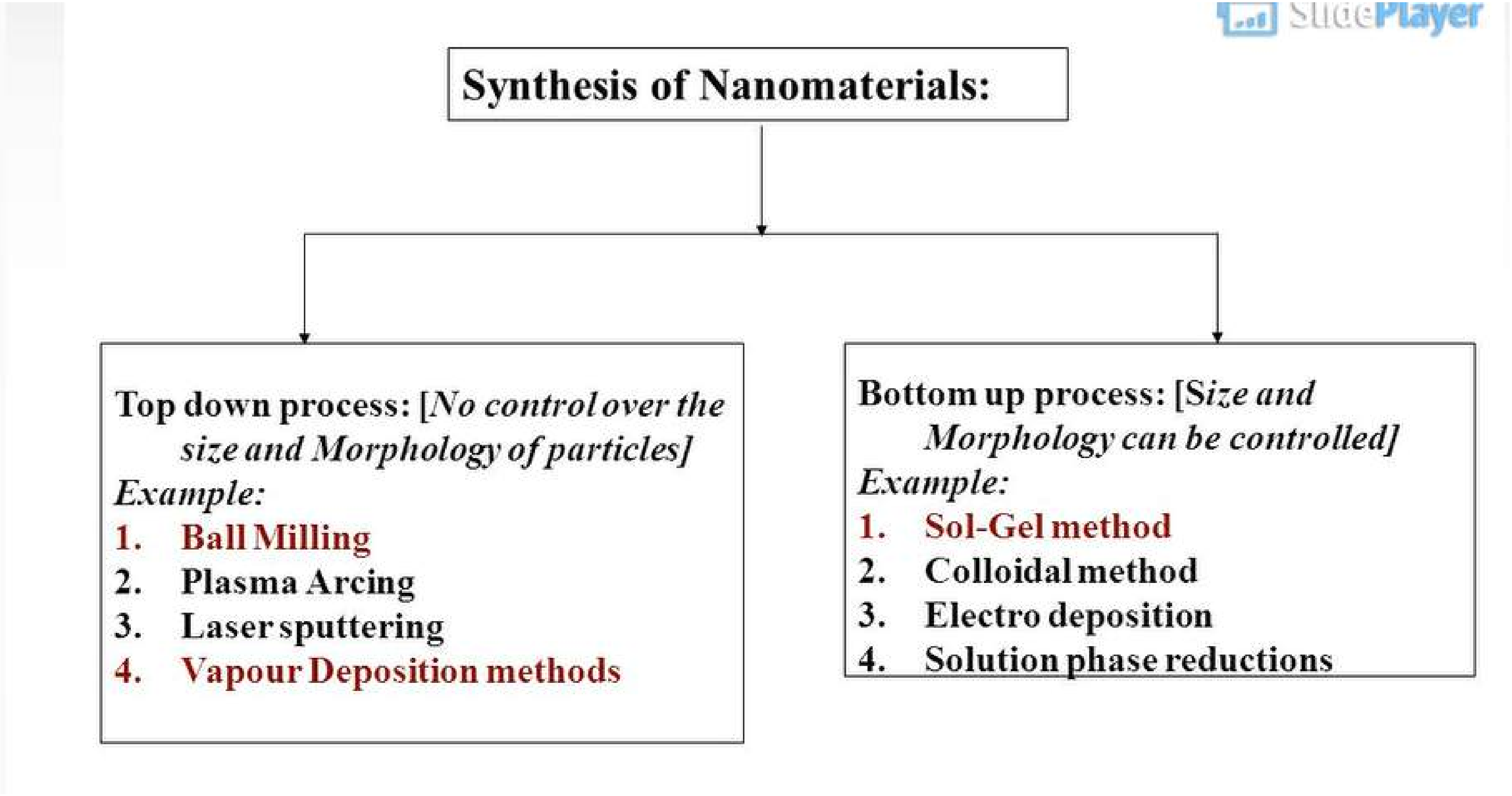
Figure 2.

Schematic diagram showing energy band structures in atom, bulk material, and quantum nanostructure.

Surface to Volume Ratio



Side of Cube	Area of side	Area of cube surface	Volume	Ration of surface area to volume
1 cm	1 cm^2	6 * 1 cm^2	1 cm^3	6/1
2 cm	4 cm^2	6 * 4 cm^2	8 cm^3	24/8 =3/1
4 cm	16 cm^2	6 * 16 cm^2	64 cm^3	96/64 = 3/2



Synthesis of Nanomaterials:

Top down process: [*No control over the size and Morphology of particles]*

Example:

1. **Ball Milling**
2. **Plasma Arcing**
3. **Laser sputtering**
4. **Vapour Deposition methods**

Bottom up process: [*Size and Morphology can be controlled]*

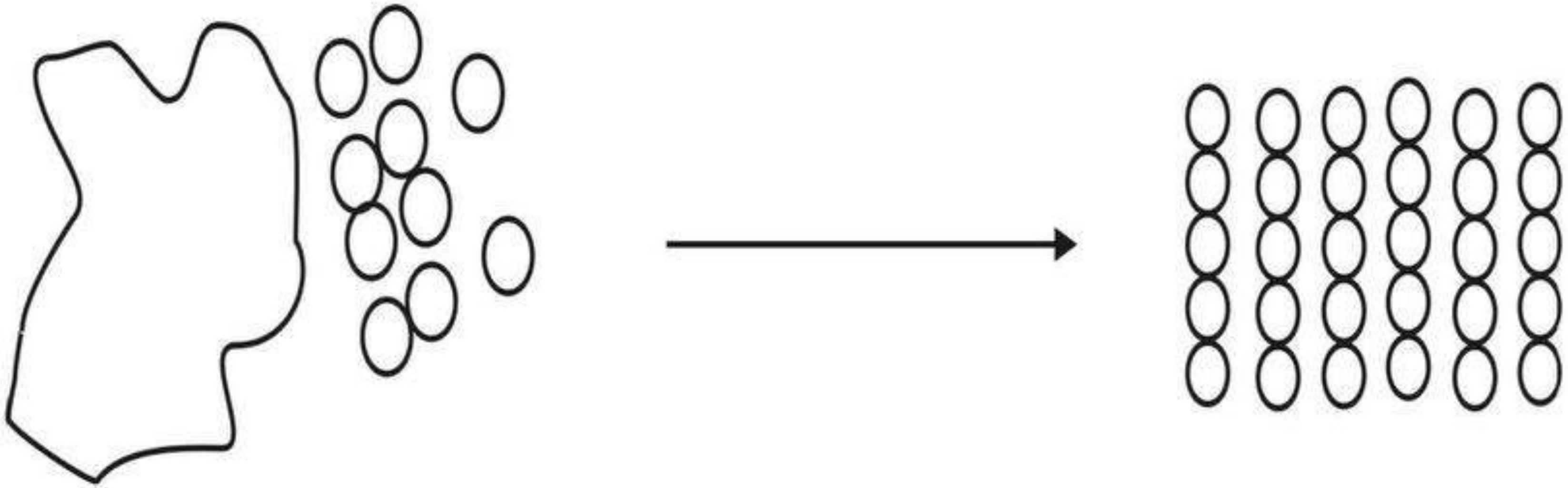
Example:

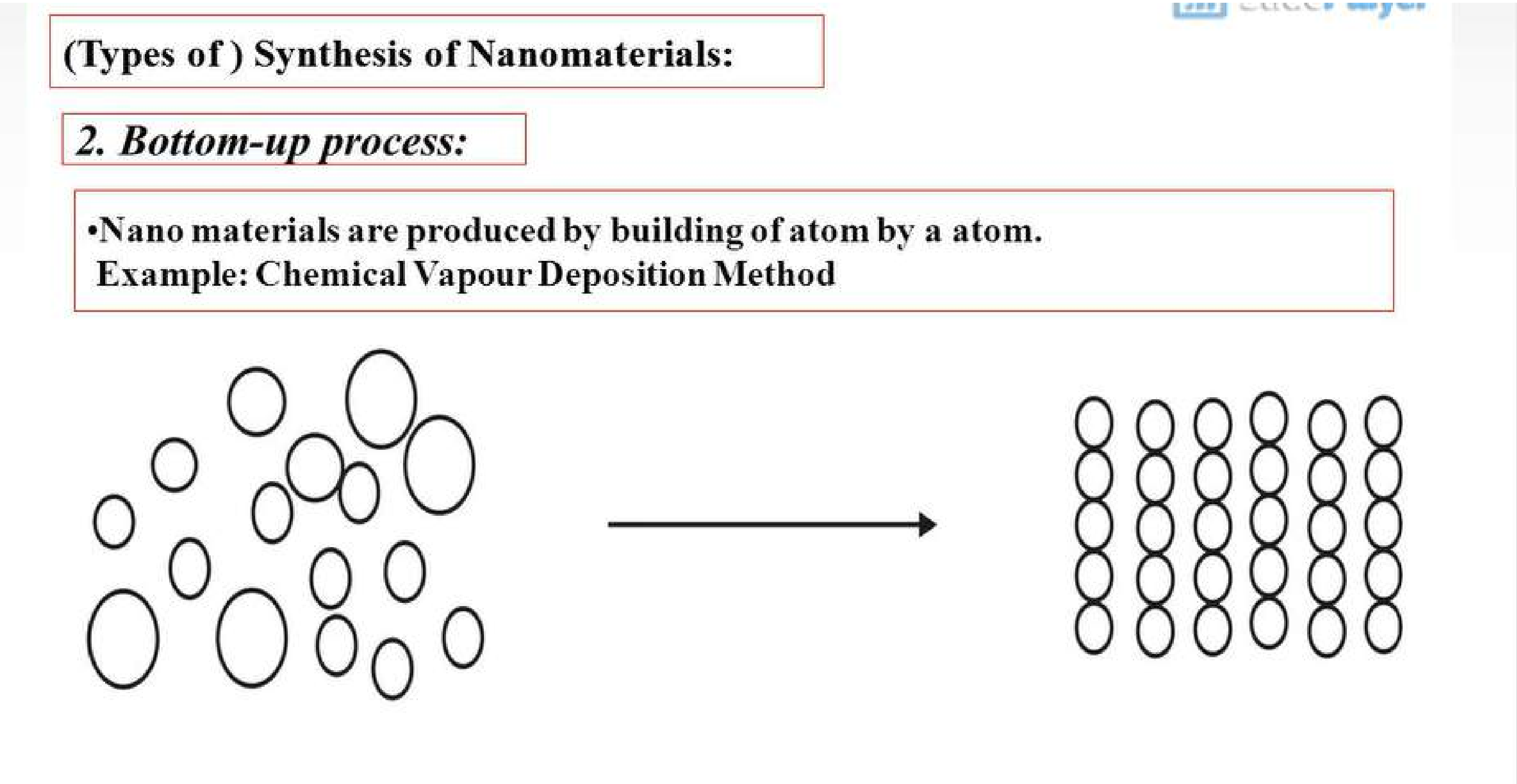
1. **Sol-Gel method**
2. **Colloidal method**
3. **Electro deposition**
4. **Solution phase reductions**

(Types of) Synthesis of Nanomaterials:

1. Top down process:

- **Bulk materials are broken into nano sized particle (for processing solid-state materials) Example: Ball milling method.**





(Types of) Synthesis of Nanomaterials:

2. Bottom-up process:

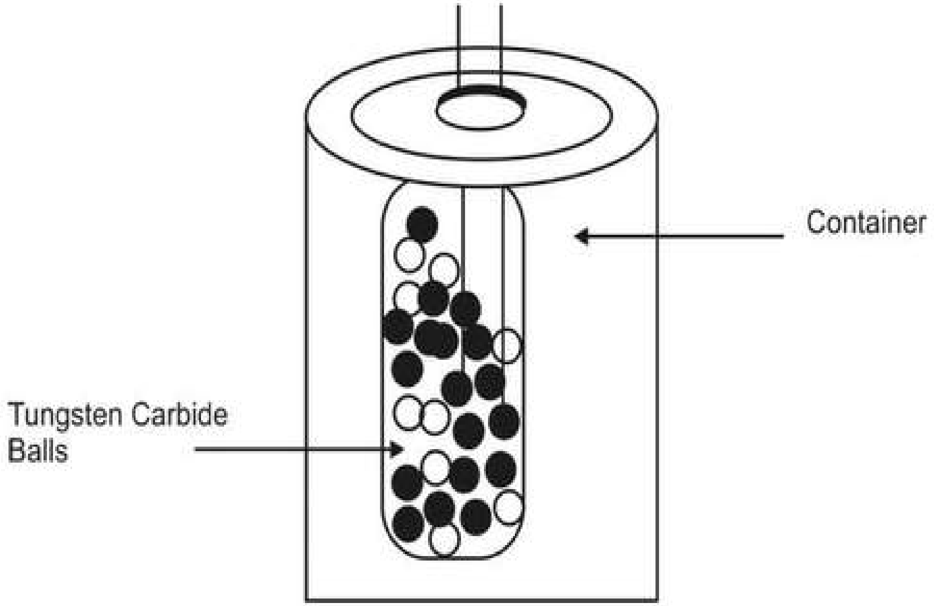
- **Nano materials are produced by building of atom by a atom.**

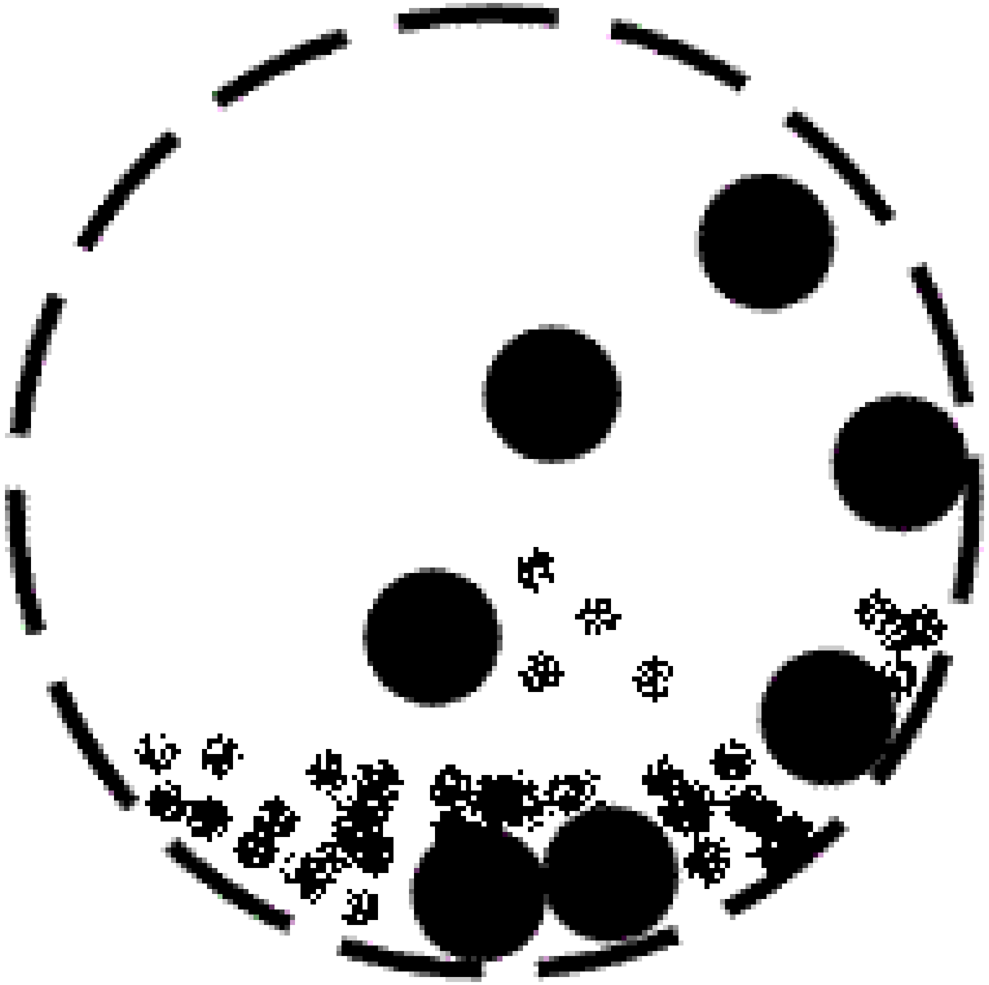
Example: Chemical Vapour Deposition Method

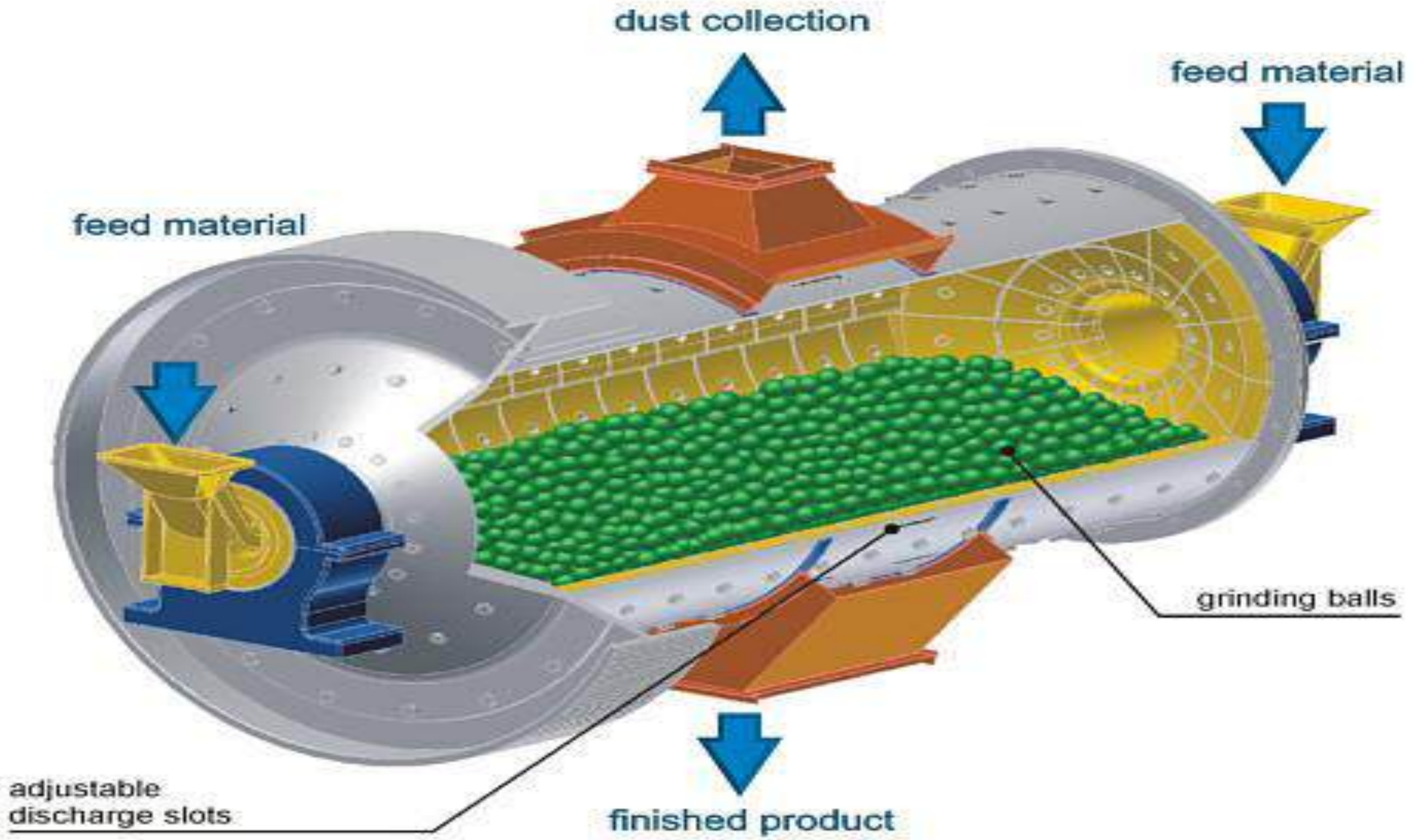
Ball Milling

Principle: Small hard balls are allowed to rotate inside a container and then it is made to fall on a solid with high force to crush the solid into nano crystal.

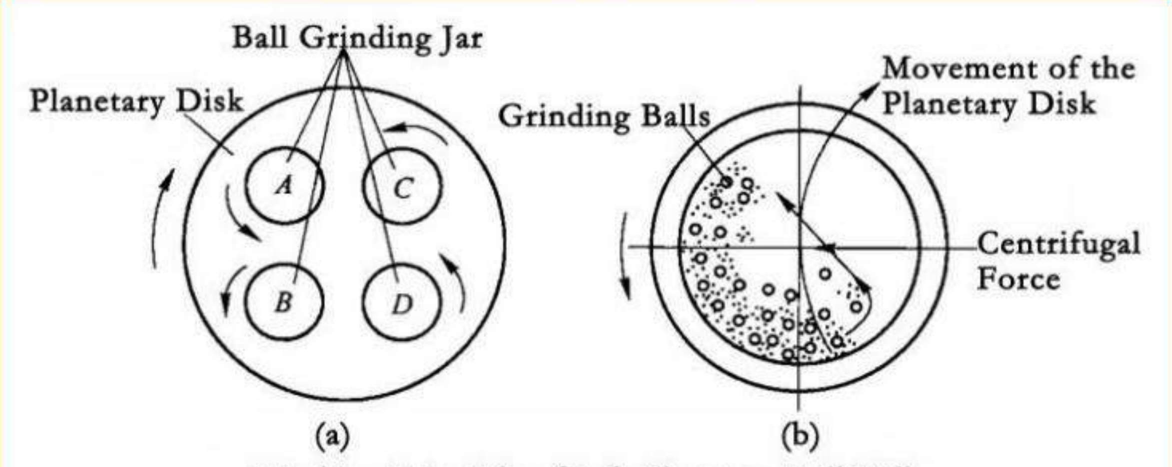
Construction and Working: Hardened steel or tungsten carbide balls are put in a container along with powder of particles (50µm) of a desired material. The container is closed with tight lids.





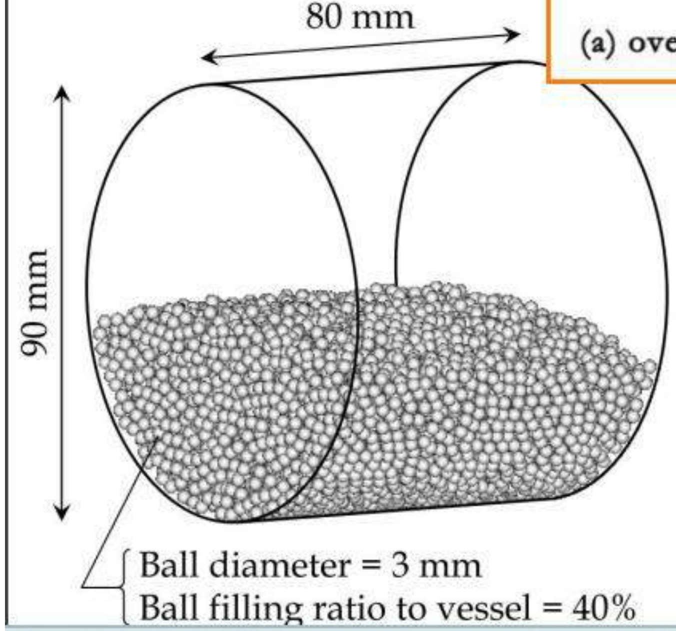

dust collection
feed material
feed material
grinding balls
adjustable
discharge slots
finished product

Raw Material Preparation: Comminution (Milling, grinding and size reduction)

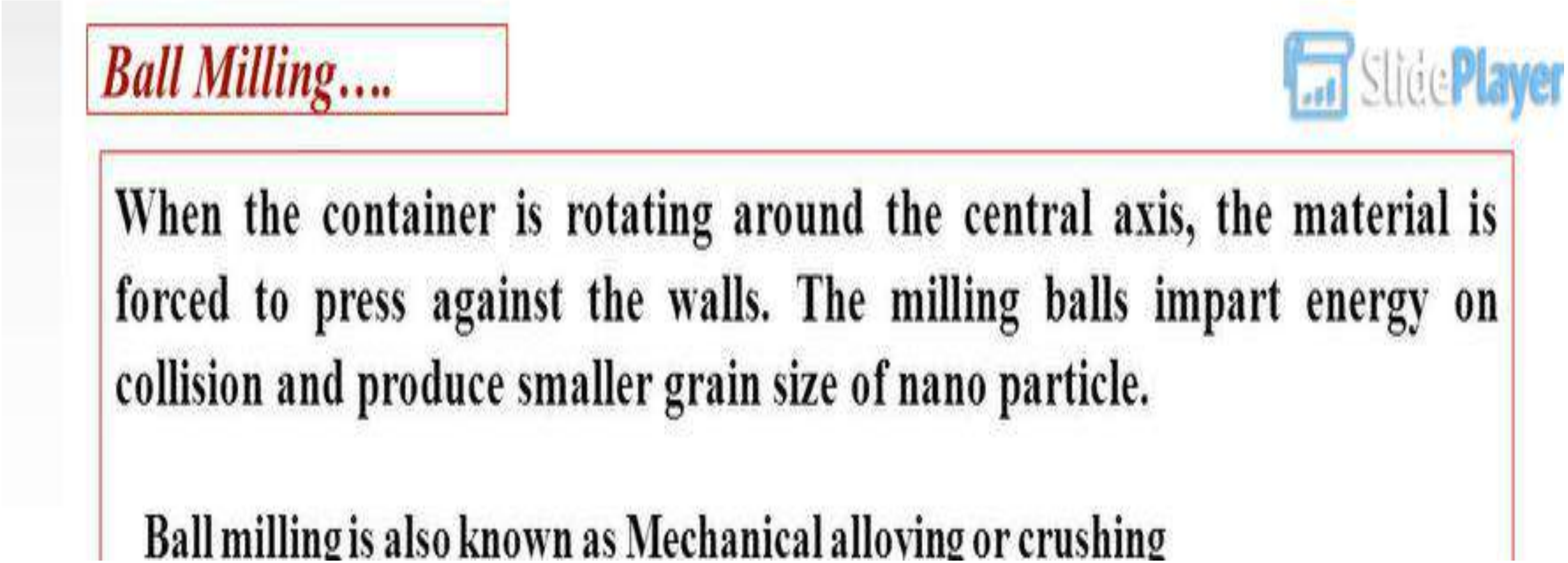


Working Principle of Lab Planetary Ball Mill

(a) overall layout of planetary disk (b) horizontal section of grinding jar



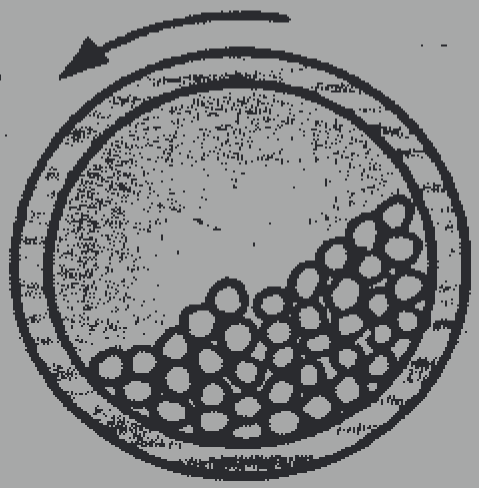
http://w.advancedmaterials.us/zirconia.htm



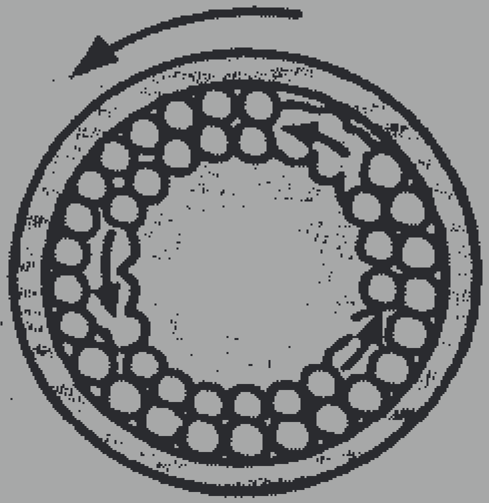
Ball Milling….

When the container is rotating around the central axis, the material is forced to press against the walls. The milling balls impart energy on collision and produce smaller grain size of nano particle.

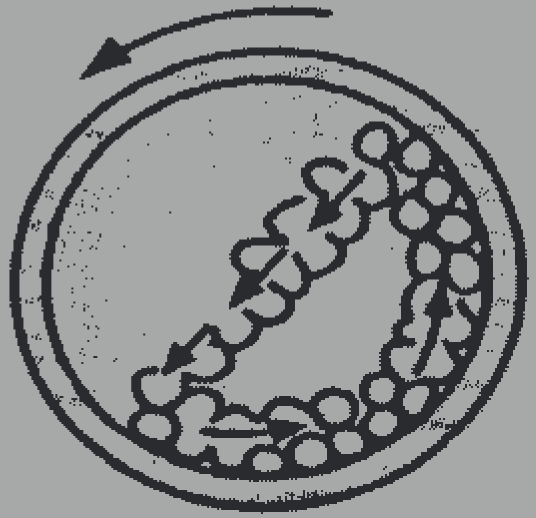
Ball milling is also known as Mechanical alloying or crushing



A
Low speed



B
High speed



C
Correct speed

Advantages of a Ball Mill : Ball mills have several advantages over other systems used for making material in the powder form. These are :

1. The cost of installation and grinding medium is low hence inexpensive process.
2. Ball milling is suitable for both batch and continuous operation
3. Ball milling is suitable for both open and closed circuit grinding
4. Material of any hardness can be grounded
5. Small particles with narrow size distribution (2 to 20 nm) can be produced.

Drackbacks of high Energy Ball Milling : Low surface, highly polydisperse size distribution and partially amorphous state of the powder. Shape of the nanomaterial is irregular. Contamination of product may occur as a result of wear and tear.

Applications

A ball mill can be used for the synthesis of nanostructured metaloxides for gas detection. It can also be used for grinding materials such as ores, chemicals, ceramic raw materials and paints etc. Grinding can be carried out either wet or dry but wet grinding is performed at low speed. Ball mills are used in pyrotechnics and the manufacture of black powder. However, it cannot be used in the preparation of some

Sol-gel Method:

This method involves two types of materials ‘Sol’ and ‘Gel’

Principle:

- Sol-Gel method involves formation of ‘sols’ in a liquid and then connecting the sol particles to form a network.
- By drying the liquid, it is possible to obtain powders, thin films etc.,

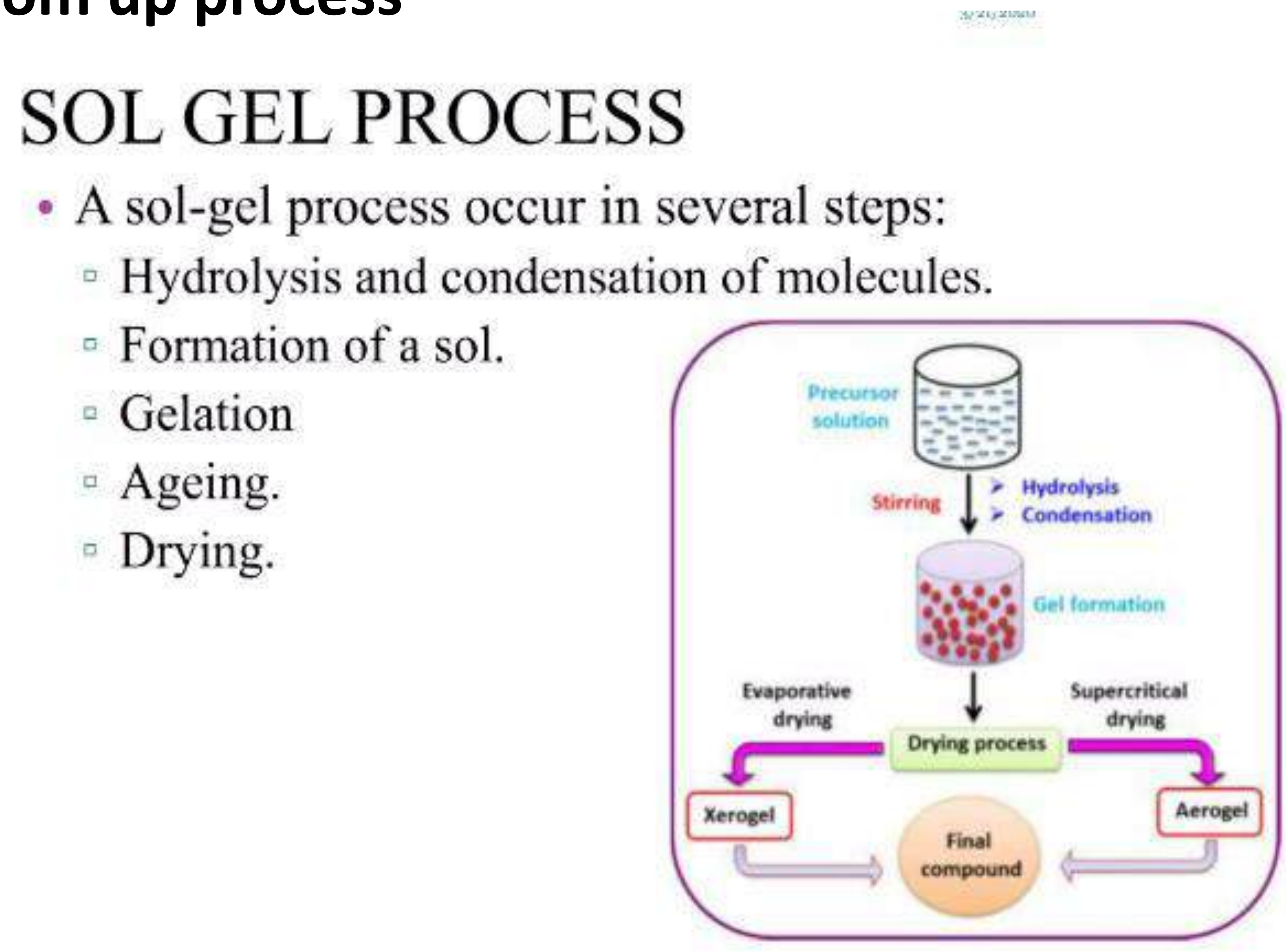
Methods for sol-gel formation:

Sol can be obtained by,

- Hydrolysis
- Condensation and Polymerization of monomers to form particles
- Agglomeration of particles

After the formation of sol, formation of network (gelation) which extends throughout the liquid medium is obtained to form a gel.

Bottom up process



SOL GEL PROCESS

- A sol-gel process occur in several steps:
  - Hydrolysis and condensation of molecules.
  - Formation of a sol.
  - Gelation
  - Ageing.
  - Drying.

Advantages of Sol gel method

- Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films.
- Obtain pure , size controlled stable and monodispersed nanoparticles ranges 20-200 nm.
- Precise control over the doping level is also easier in this process

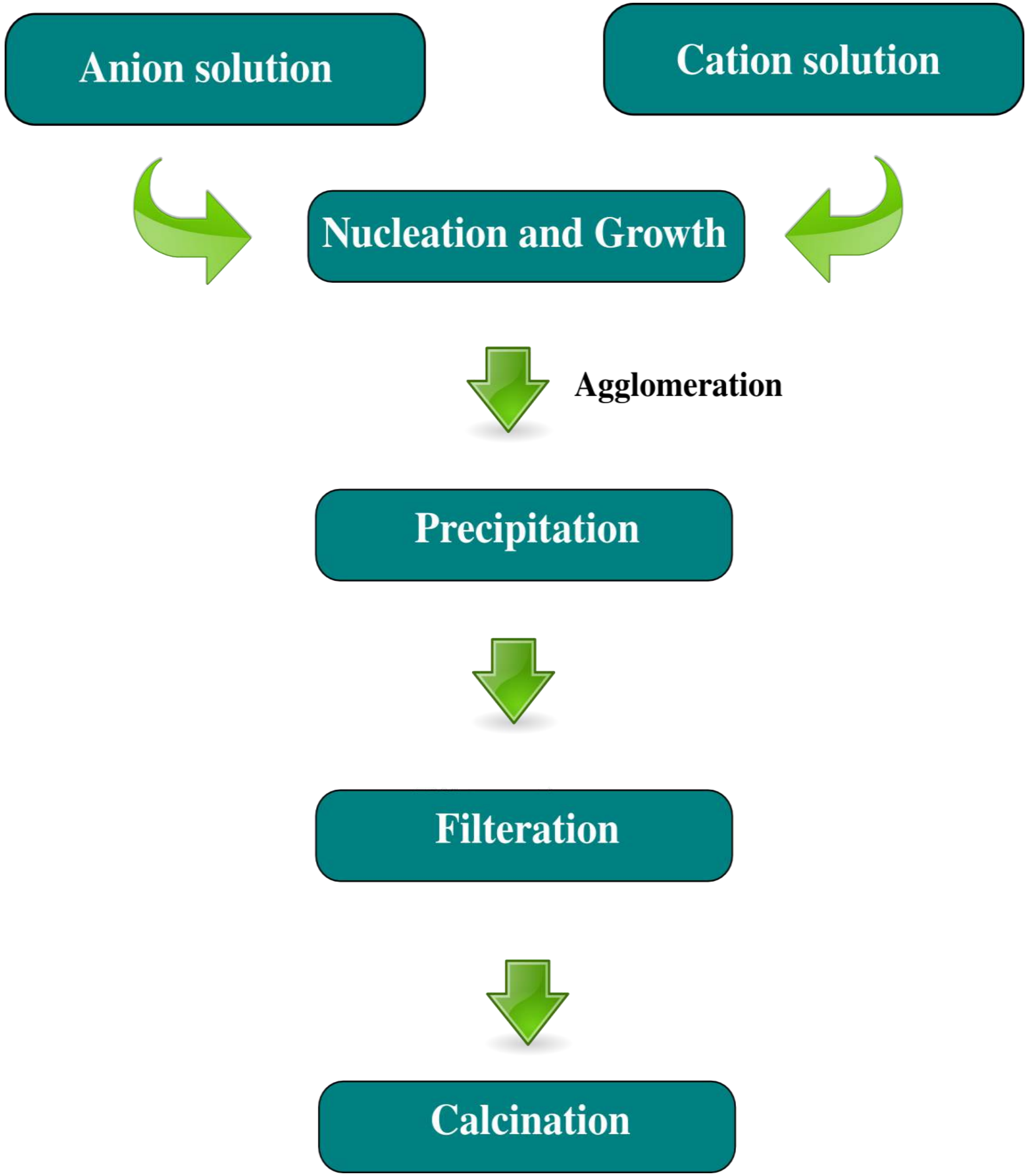
Disadvantages of Sol gel method

- This technique is quite substrate dependent.
- Metal alkoxides are the most preferred precursor. But they are expensive.
- We have little control over porosity of the gel which inturn affects the rate of solvent removal from the gel in order to form the final powder.
- Formation of gel is a slow process, which makes sol gel a time consuming fabrication technique as compared to other methods (combustion synthesis).

Synthesis by co-precipitation Technique

- It is a technique based on the transfer of a precipitate of substances that are usually dissolved under the significant influence under the conditions that are employed.
- It is a simple, economical, and industrially viable technique that can be used for the synthesis of technologically important oxide materials. It can be possible to synthesize powders without any additional agglomeration steps.
- One can tailor the process to get nano size particles by adjusting pH temperature and solvents. It is a low cost and high yield synthesis technique.

Co-precipitation Bottom up process



Anion solution

Cation solution

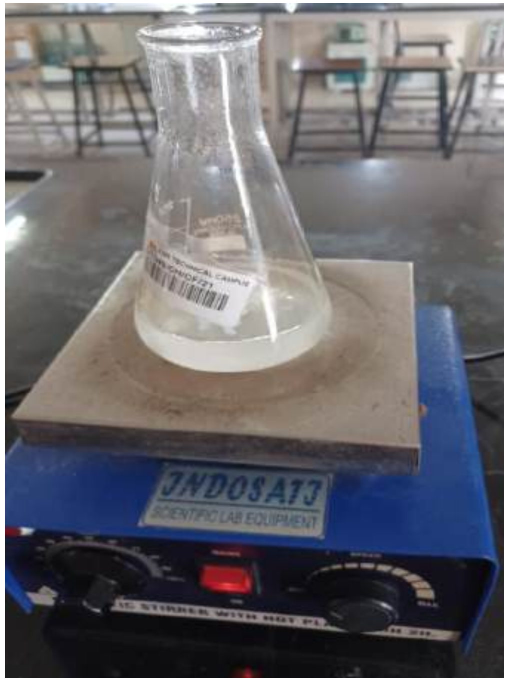
Nucleation and Growth

Agglomeration

Precipitation

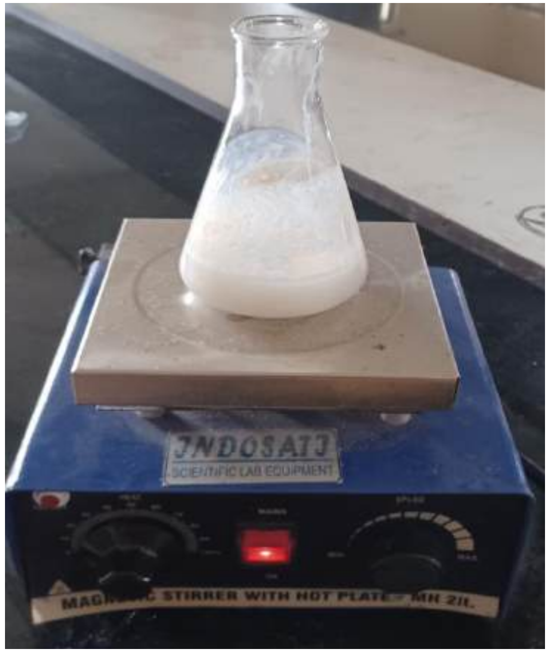
Filteration

Calcination



Anion solution

cation solution



After mixing
precipitate formed

Filteration

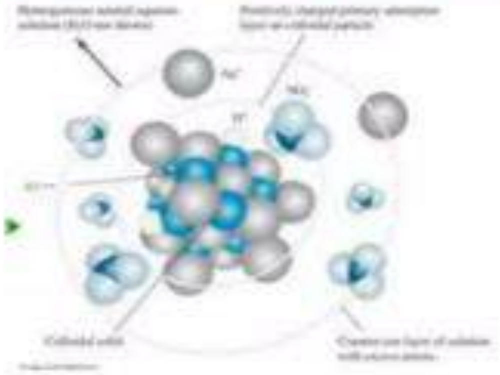
Types of coprecipitation

There are four types of coprecipitation:
(1) surface adsorption,
(2) mixed-crystal formation,
(3) occlusion, and
(4) mechanical entrapment.

(1) & (2) are equilibrium processes, while (3) & (4) arise from kinetics of crystal growth.

Surface Adsorption

- Adsorption is a common source of coprecipitation that is likely to cause significant contamination of precipitates with large specific surface areas (coagulated colloids).
- Coagulation of a colloid does not significantly decrease the amount of adsorption.
- The net effect of surface adsorption is therefore the carrying down of an otherwise soluble compound as a surface contaminant.
- Ex. Coagulated silver chloride is contaminated with primarily adsorbed Ag+ along with nitrate or other anions.

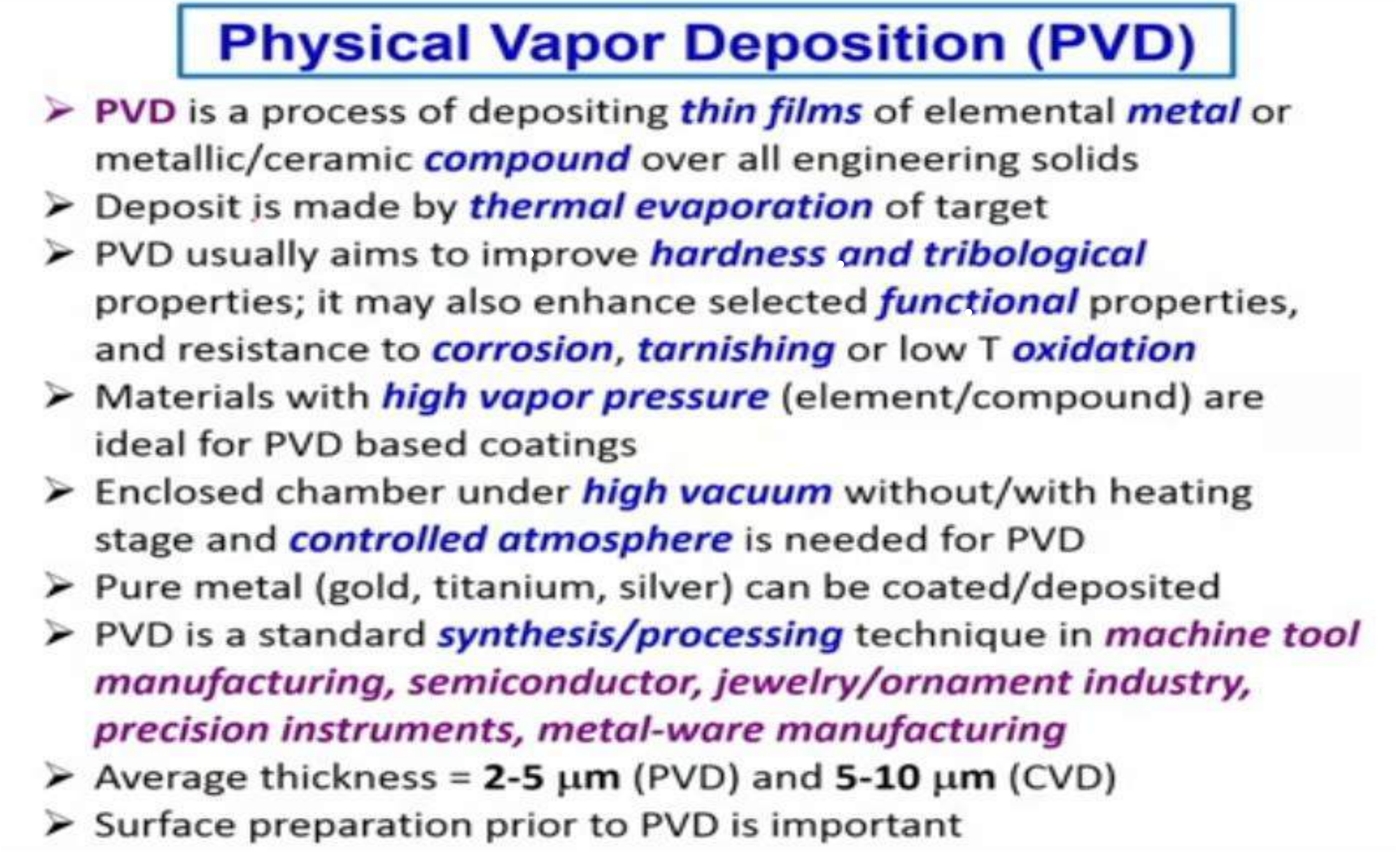


Mixed-Crystal Formation

- In mixed-crystal formation, one of the ions in the crystal lattice of a solid is replaced by an ion of another element.
- The extent of mixed-crystal contamination is governed by the law of mass action and increases as the ratio of contaminant to analyte concentration increases.

Occlusion and Mechanical Entrapment:

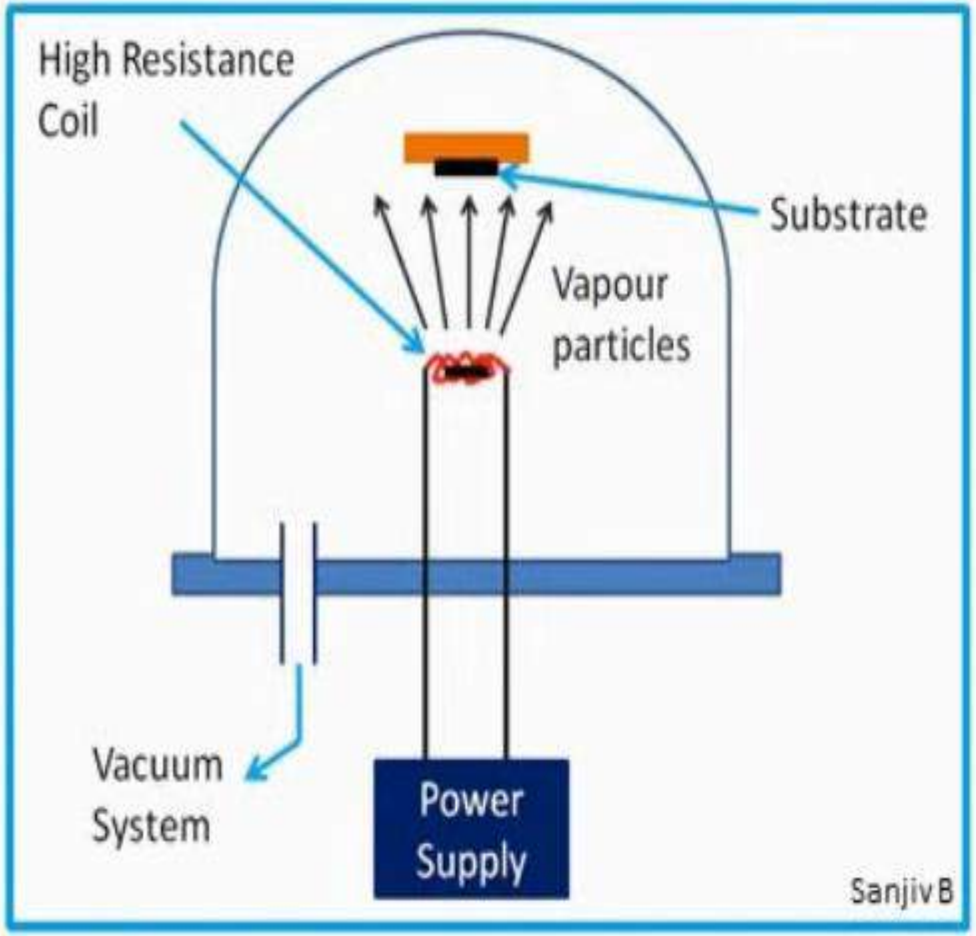
- When a crystal is growing rapidly during precipitate formation, foreign ions in the counter-ion layer may become trapped, or occluded, within the growing crystal.
- Occlusion is a type of coprecipitation in which a compound is trapped within a pocket formed during rapid crystal growth
- Mixed-crystal formation may occur in both colloidal and crystalline precipitates, whereas occlusion and mechanical entrapment are confined to crystalline precipitates.
- Mechanical entrapment occurs when crystals lie close together during growth.
- Both occlusion and mechanical entrapment are at a minimum when the rate of precipitate formation is low, that is, under conditions of low supersaturation.
- In addition, digestion is often remarkably helpful in reducing these types of coprecipitation.



Physical Vapor Deposition (PVD)

- **PVD** is a process of depositing ***thin films*** of elemental ***metal*** or metallic/ceramic ***compound*** over all engineering solids
- Deposit is made by ***thermal evaporation*** of target
- PVD usually aims to improve ***hardness and tribological*** properties; it may also enhance selected ***functional*** properties, and resistance to ***corrosion***, ***tarnishing*** or low T ***oxidation***
- Materials with ***high vapor pressure*** (element/compound) are ideal for PVD based coatings
- Enclosed chamber under ***high vacuum*** without/with heating stage and ***controlled atmosphere*** is needed for PVD
- Pure metal (gold, titanium, silver) can be coated/deposited
- PVD is a standard ***synthesis/processing*** technique in ***machine tool manufacturing, semiconductor, jewelry/ornament industry, precision instruments, metal-ware manufacturing***
- Average thickness = **2-5 μm** (PVD) and **5-10 μm** (CVD)
- Surface preparation prior to PVD is important

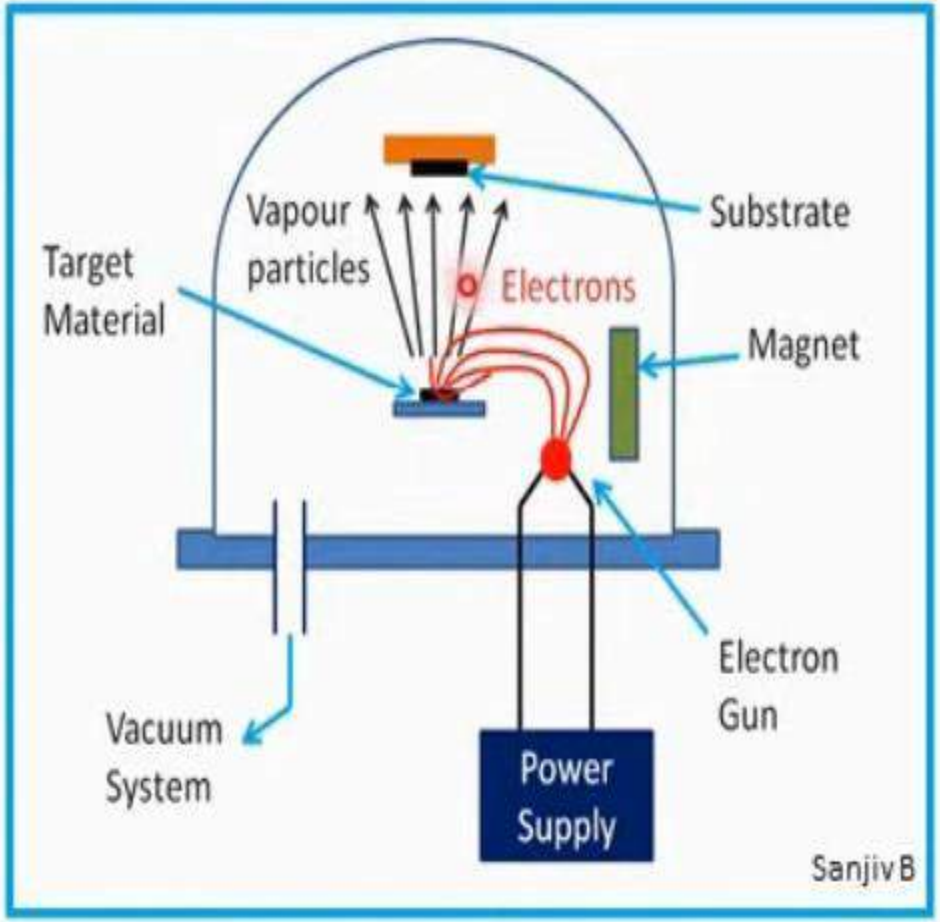
Physical Vapour Deposition Method (Resistive Method)



- Bottom-up Approach.
- The material is evaporated in a vacuum.
- Vapour particles travel towards the cold target (substrate) Deposited and condense back to a solid state.
- Resistance evaporators

heat is generated to evaporate the material by passing current through a high resistance coil.

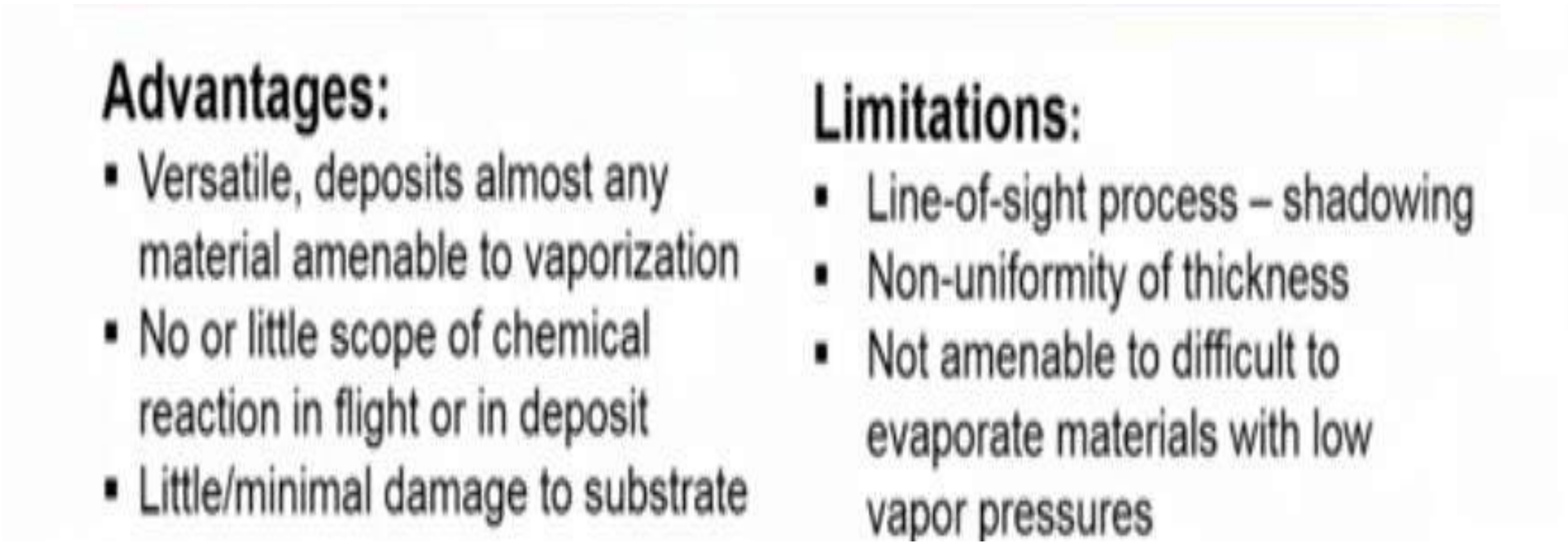
Physical Vapour Deposition Method (Sputtering Method)



Sanjiv B

- Bottom-up Approach.
- The material is evaporated in a vacuum.
- Vapour particles travel towards the cold target (substrate) Deposited and condense back to a solid state.
- Sputtering evaporators

atoms are ejected from a solid target due to bombardment of the target by energetic electrons.



Advantages:

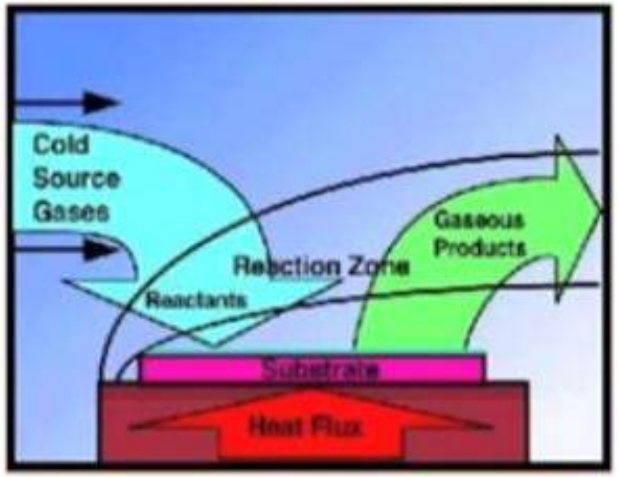
- Versatile, deposits almost any material amenable to vaporization
- No or little scope of chemical reaction in flight or in deposit
- Little/minimal damage to substrate

Limitations:

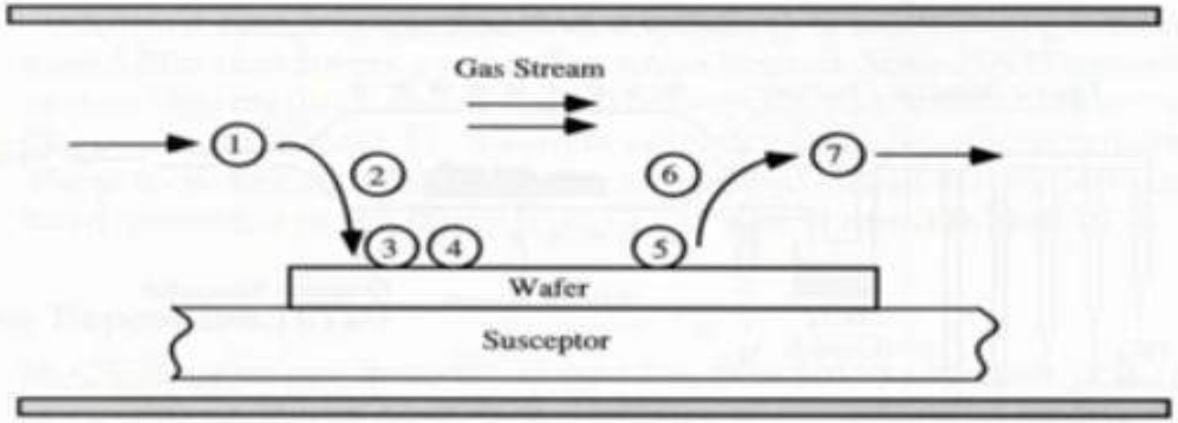
- Line-of-sight process – shadowing
- Non-uniformity of thickness
- Not amenable to difficult to evaporate materials with low vapor pressures

Chemical Vapor Deposition (CVD)

- **CVD** involves formation of ***non-volatile thin solid film*** by ***reaction of ions/species in the vapor state*** and subsequent deposition
- Reactant gases ***decompose and react*** on heated surface to form thin film
- CVD involves exposing the heated substrate to one or more volatile precursors, which react ***on the substrate surface*** to produce the film
- CVD is a very ***versatile process*** to produce ***coatings, powders, fibers and monolithic*** parts
- CVD can produce almost any metallic/non-metallic element like ***C and Si,*** and compounds like ***carbides, nitrides, borides, oxides, intermetallics***
- CVD is widely used in the ***semiconductor industry***, as part of semiconductor ***device fabrication process***, to deposit various films including: ***polycrystalline, amorphous, and epitaxial Si, SiO_2, Si-Ge, W, Si_3N_4, silicon oxynitride, titanium nitride***, various ***high-k dielectric*** materials
- CVD can also produce ***synthetic diamond, diamond like coating, cubic-BN,*** etc.

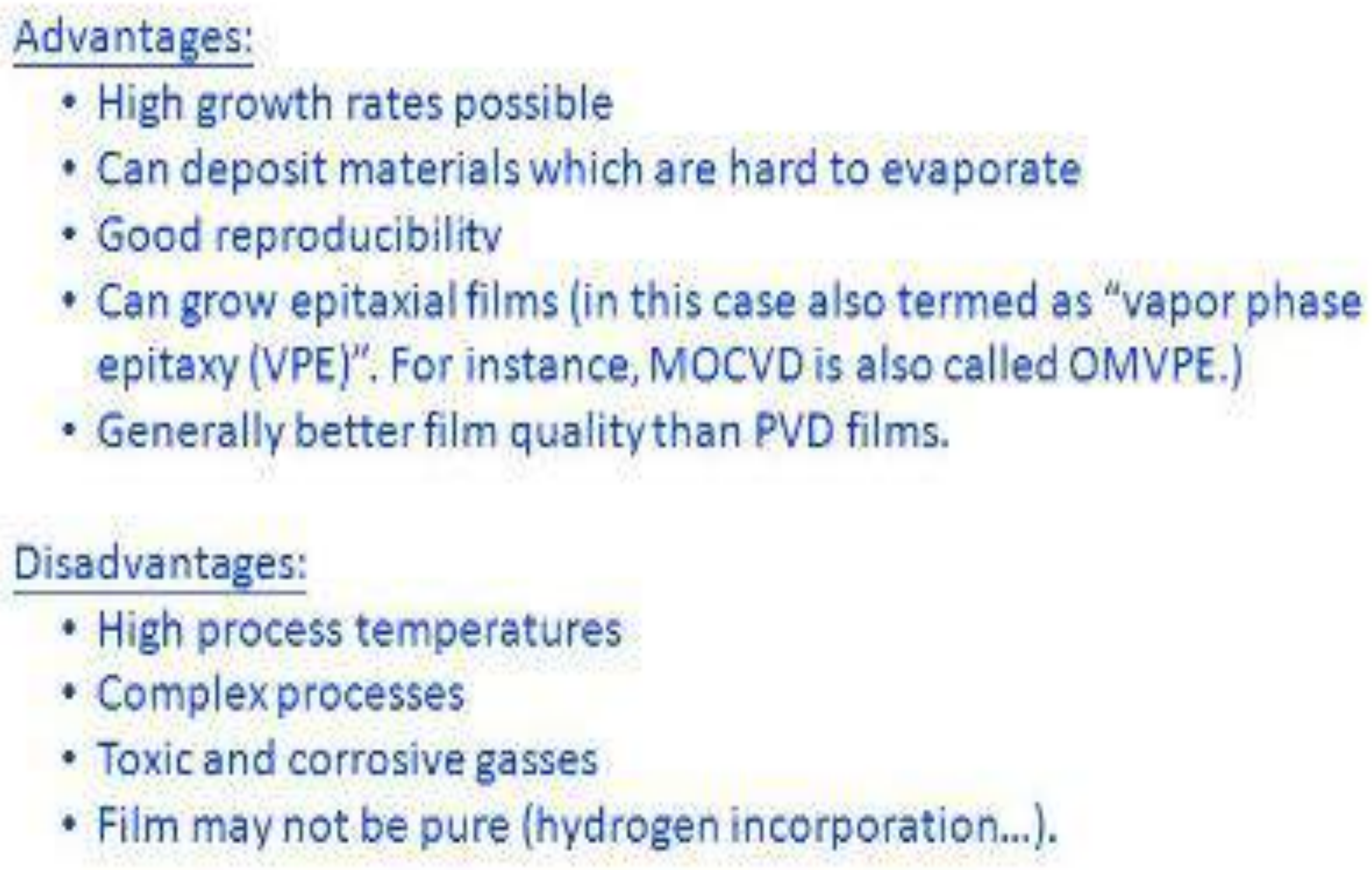


Steps in CVD



PROCESS STEPS in CVD:

1. Transport of reactants via **forced convection** to reaction region
2. Transport of reactants via **diffusion** to wafer surface
3. **Adsorb** reactants on surface
4. **Surface processes**: ***chemical decomposition, surface migration, site incorporation***, etc.
5. **Desorption** of by-products from surface
6. **Transport of byproducts** through *boundary layer*
7. Transport of byproducts **away from deposition region**

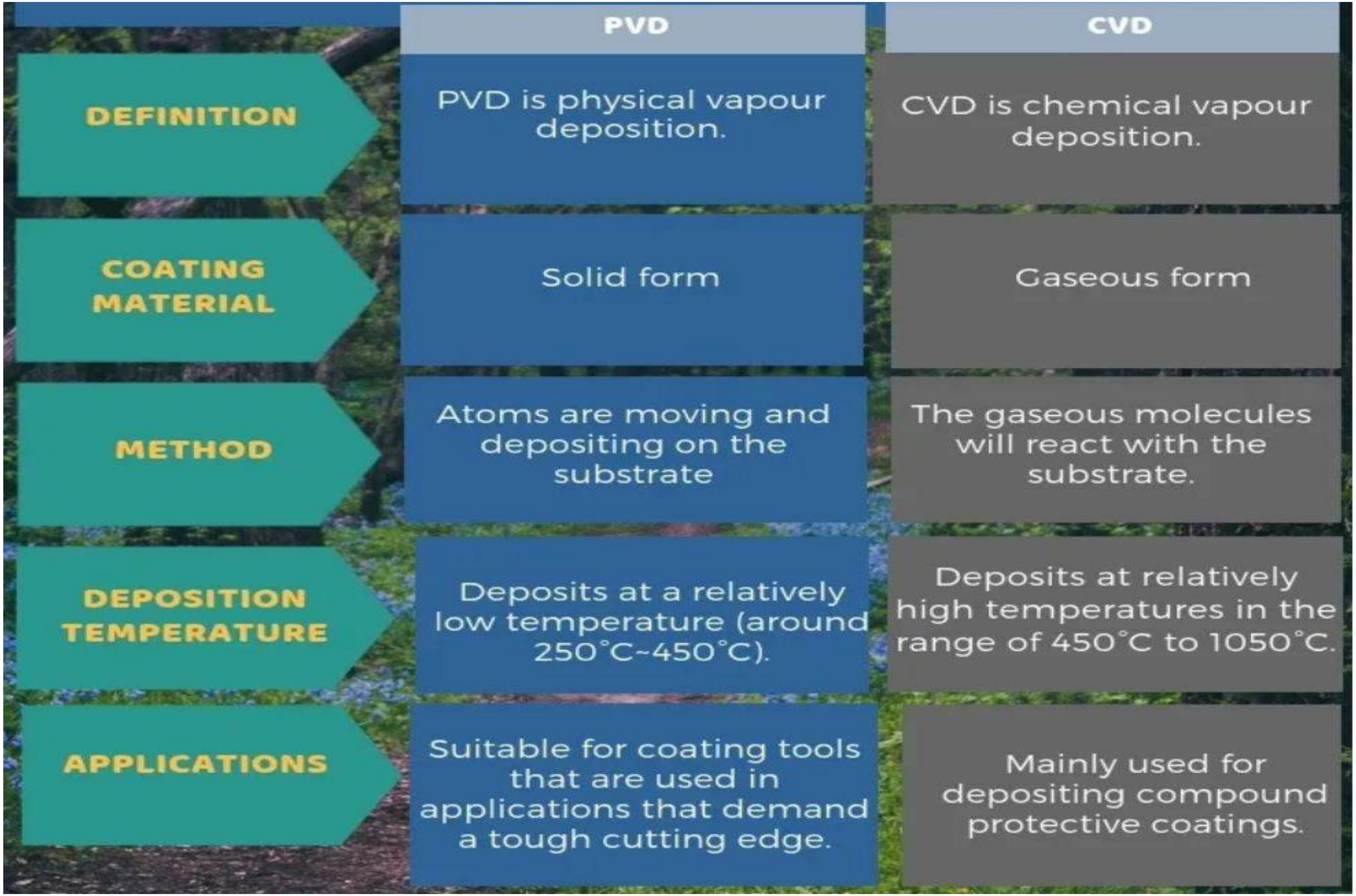


Advantages:

- High growth rates possible
- Can deposit materials which are hard to evaporate
- Good reproducibility
- Can grow epitaxial films (in this case also termed as "vapor phase epitaxy (VPE)". For instance, MOCVD is also called OMVPE.)
- Generally better film quality than PVD films.

Disadvantages:

- High process temperatures
- Complex processes
- Toxic and corrosive gasses
- Film may not be pure (hydrogen incorporation...).



	PVD	CVD
DEFINITION	PVD is physical vapour deposition.	CVD is chemical vapour deposition.
COATING MATERIAL	Solid form	Gaseous form
METHOD	Atoms are moving and depositing on the substrate	The gaseous molecules will react with the substrate.
DEPOSITION TEMPERATURE	Deposits at a relatively low temperature (around 250°C~450°C).	Deposits at relatively high temperatures in the range of 450°C to 1050°C.
APPLICATIONS	Suitable for coating tools that are used in applications that demand a tough cutting edge.	Mainly used for depositing compound protective coatings.

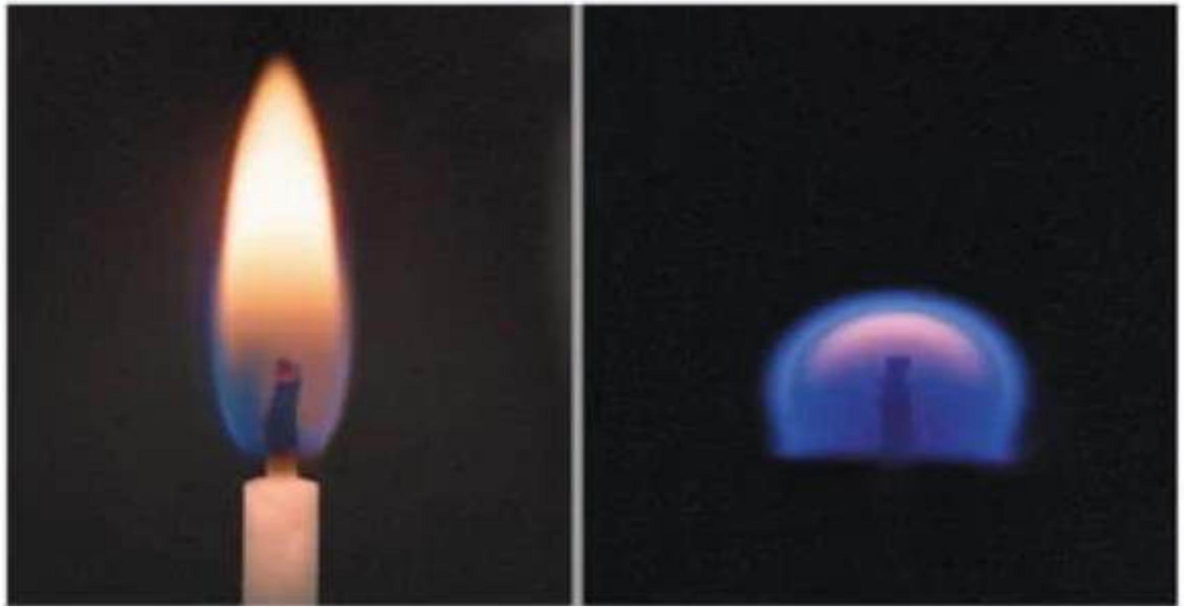
2) Combustion :-

The chemical process in which a substance reacts with oxygen to produce heat is called combustion.

The substance which undergoes combustion is called a combustible substance. It is also called a fuel.

Sometimes light is also produced during combustion either as a flame or as a glow.

Air is necessary for combustion.



1) Combustible substances :-

Substances which burn in air to produce heat and light are called combustible substances.

Eg :- wood, coal, charcoal, kerosene, petrol, diesel, liquified petroleum gas (LPG), compressed natural gas (CNG) etc.

Wood

Coal

LPG

Kerosene