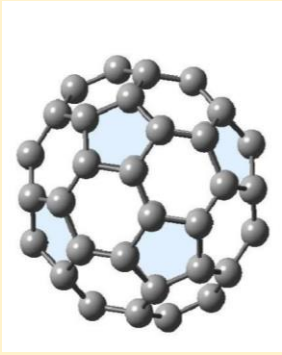


NANO – LECTURE 4



Nano Science and Nanotechnology

Synthesis of Nanomaterials

Dr. Mervat Kadhem

**Top-Down and Bottom-up
Techniques**

Synthesis of Nanomaterials

- There are different ways of classifying the synthesis routes for nanostructured materials.
- **One of them is based on the starting state of material, namely, gas, liquid and solid.**
- Techniques such as vapour condensation [physical vapour deposition (PVD) and chemical vapour deposition (CVD) and variants of these techniques] use the gaseous state of matter as the starting material for synthesizing nanoparticles.

Two Approaches

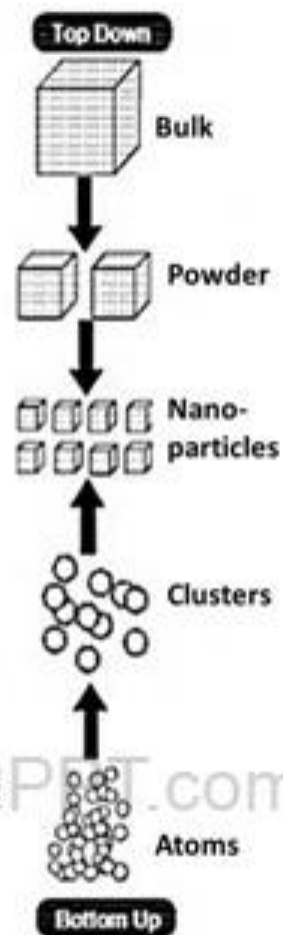
- There are two approaches, **top-down** approach and **bottom-up** approach, for the synthesis of nanomaterials and nanostructures.
- In the **top-down** approach, a suitable starting material is reduced in size using **mechanical or chemical means**
- Bottom-up approach refers to the building of a **structure atom-by-atom, molecule-by-molecule, or cluster-by-cluster**. In this approach, initially the nanostructured building blocks (i.e., nanoparticles) are formed and, subsequently, assembled into the final material **using chemical or biological procedures**.

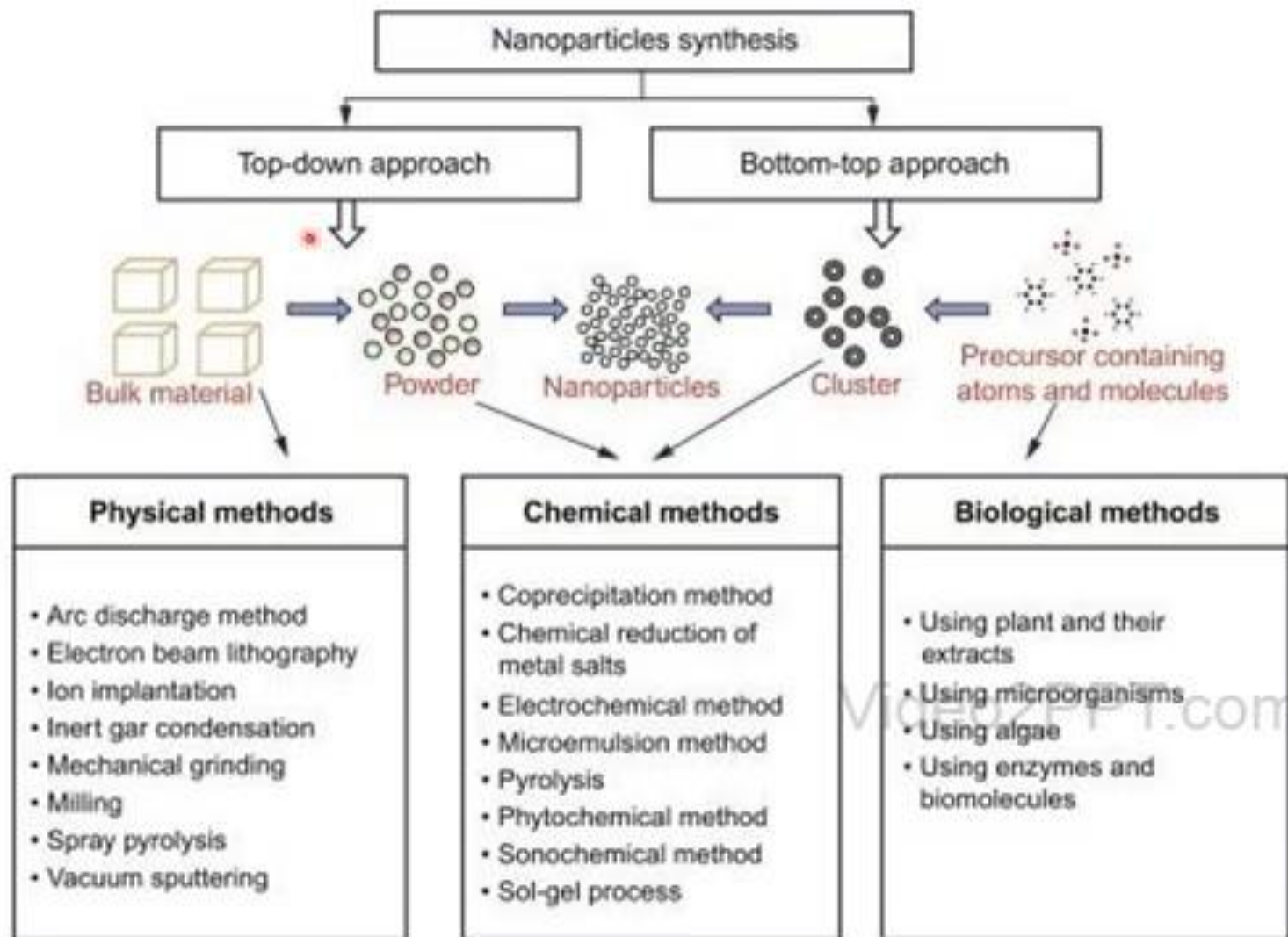
Top-down Approach

- Begins with a pattern generated on a larger scale, then reduced to nanoscale
- Relatively expensive and time consuming technique
- The approach use larger (macroscopic) initial structures
- The structures can be externally-controlled in the processing of nanostructures

Bottom-up Approach

- Start with atoms or molecules and build up to nanostructures
- Fabrication is much less expensive
- Includes the miniturization of materials components (atomic level) leading to formation of nano structures.
- During Self assembly the physical forces operating at nanoscale are used to combine basic units into larger stable structure





Top-down Approach

- In Top-down techniques, the starting material is solid state
(Physical processing methods)

ADVANTAGES

- Large scale production: deposition over a large substrate is possible
- Chemical purification is not required

DISADVANTAGES

- broad size distribution (10-1000 nm)
- varied particle shapes or geometry
- Control over deposition parameters is difficult to achieve
- Impurities: stresses, defects and imperfections get introduced
- Expensive technique

Bottom –up Approach

- All the Bottom-up techniques, the starting material is either gaseous state or liquid state of matter

ADVANTAGES

- Ultra-fine nanoparticles, nanoshells, nanotubes can be prepared
- Deposition parameters can be controlled
- Narrow size distribution is possible (1-20 nm)
- Cheaper technique

• DISADVANTAGES

- Large scale production is difficult
- Chemical purification of nanoparticles is required

Top-Down Approaches

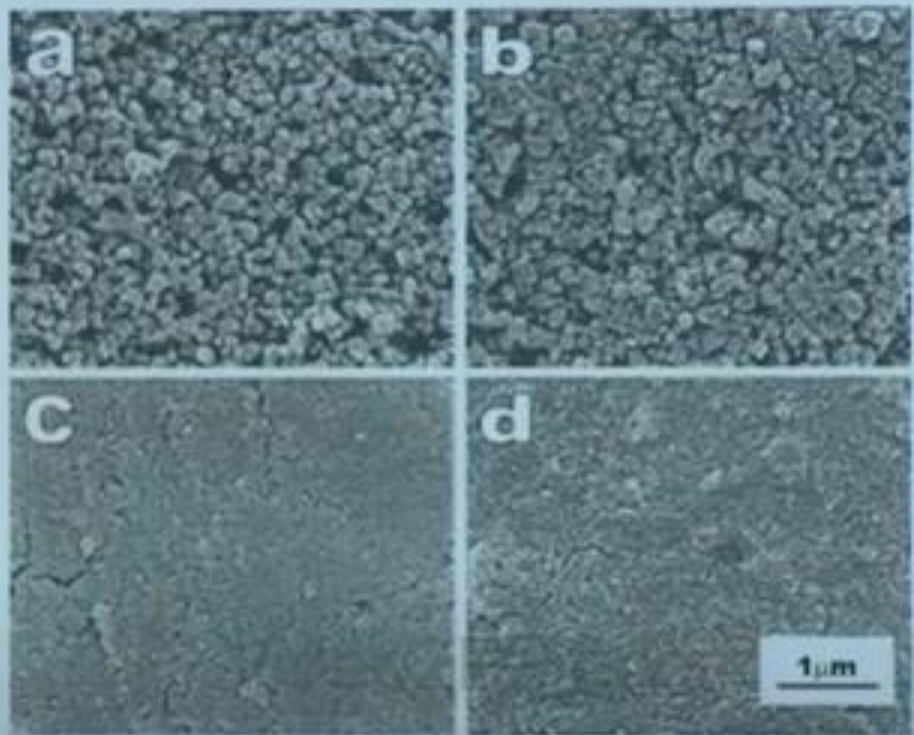
- **Ball milling:** High-energy ball milling is one of the simplest methods to synthesize NPs of metals, alloys, and composites.
- **Laser Ablation Method:** Laser is used for making metal nanoparticles
- **Lithography:** Lithography is the process of transferring a pattern into a reactive polymer film (i.e., resist)

BALL MILLING

- Ball milling is a method of production of nanomaterials
- The balls rotate with high energy inside a container and then fall on the solid with gravity force and kinetic energy and hence crush the solid into Nano-crystallites.
- This process is used in producing metallic and ceramic nanomaterials



Ball Milled powders : Scanning electron microscope images

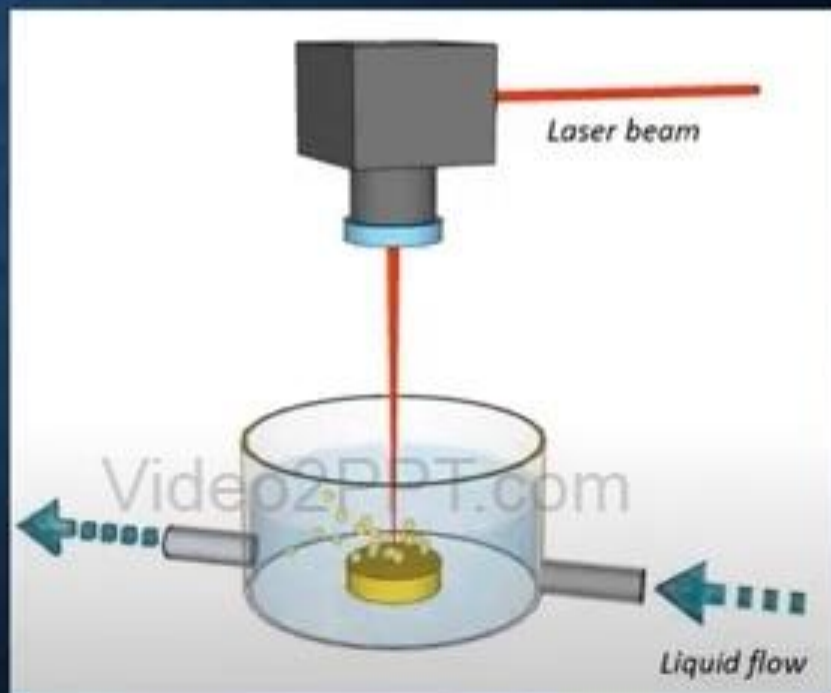


(a) 3 hours (b) 9 hours (c) 15 Hours (d) 20 hours

Laser Ablation Method

Laser Ablation

- Ag or Cu NPs by LA, a high purity Ag or Cu slice is placed at the bottom of glass vessel containing distilled water.
- It is irradiated with continuous or pulsed laser
- Results in a yellow colour of Ag and light green colour of copper colloidal solution.



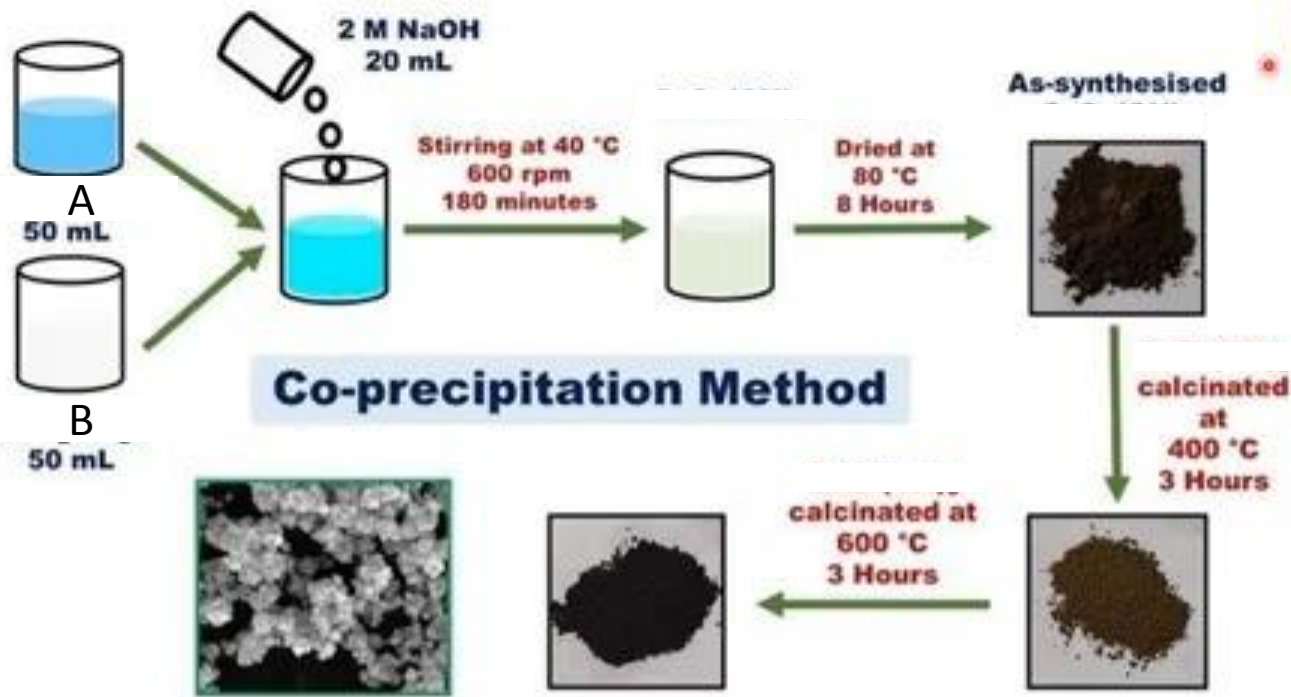
Synthesis: Bottom Up Techniques

- 1. Liquid-phase synthesis**
- 2. Gas-phase synthesis**
- 3. Vapor-phase synthesis**

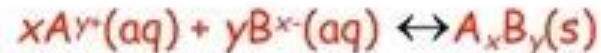
1. Liquid-Phase Synthesis

- Coprecipitation
- Sol-gel Processing
- Microemulsions
- Hydrothermal/Solvothermal Synthesis
- Microwave Synthesis

Coprecipitation



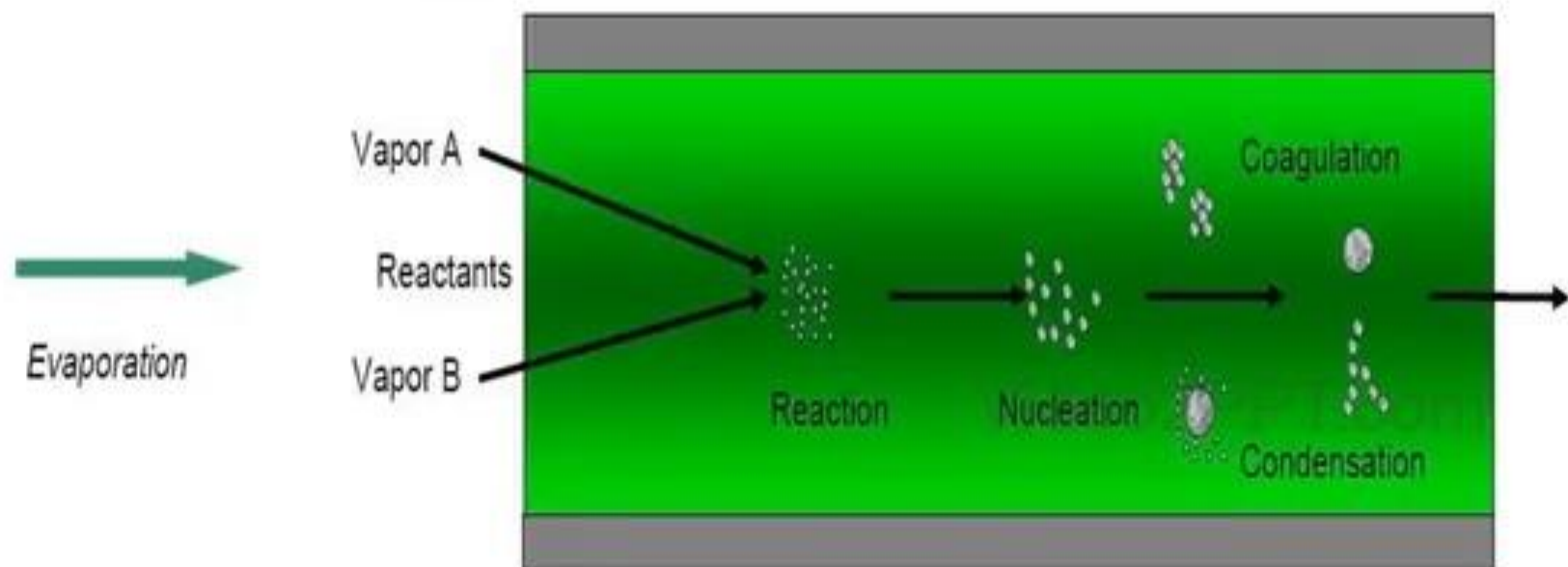
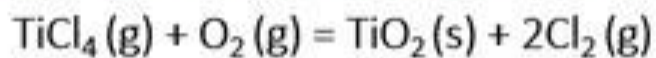
Schematic diagram of co-precipitation method for synthesis of nanoparticles



2. Gas-Phase Synthesis

Cooling of a saturated dense gas under specific conditions induces nucleation and growth of nanoparticles

Example: Gas Phase Chemical Preparation of TiO_2



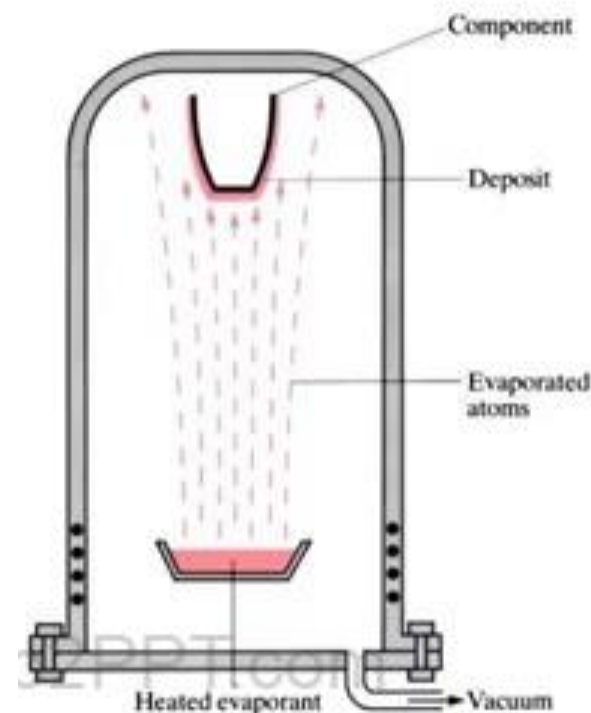
3. Vapour Phase Synthesis

Physical Vapor Deposition (PVD)

- Physical vapor deposition (PVD) is a process of transferring growth species from a source or target and depositing them on a substrate to form a **thin film**.
- PVD methods can be categorized into two groups, **evaporation** and **sputtering**, based on source of removing the species from the target. In evaporation, the growth species are removed from the source by thermal means, while in sputtering, atoms or molecules are dislodged from solid target through impact of plasma.
- Deposition of thin films by evaporation is carried out at a **low pressure** (10^{-3} – 10^{-10} torr), and therefore, atoms and molecules in the vapor phase are not collided with each other prior to arrival at the substrate since the mean free path is very large as compared to the source-to-substrate distance. Therefore, the **film quality** is relatively poor.
- The **pulsed laser beams/sputtering** can reduce this problem to a certain extent

Physical Vapor Deposition (PVD)

- Physical vapor deposition (PVD) refers to a family of processes in which a material is converted to its vapor phase in a vacuum chamber and condensed onto a substrate surface as a *thin film*.
- PVD can be used to produce coatings of a wide variety of materials:
 - metals
 - alloys
 - ceramics
 - glasses
 - semiconductors
 - polymers

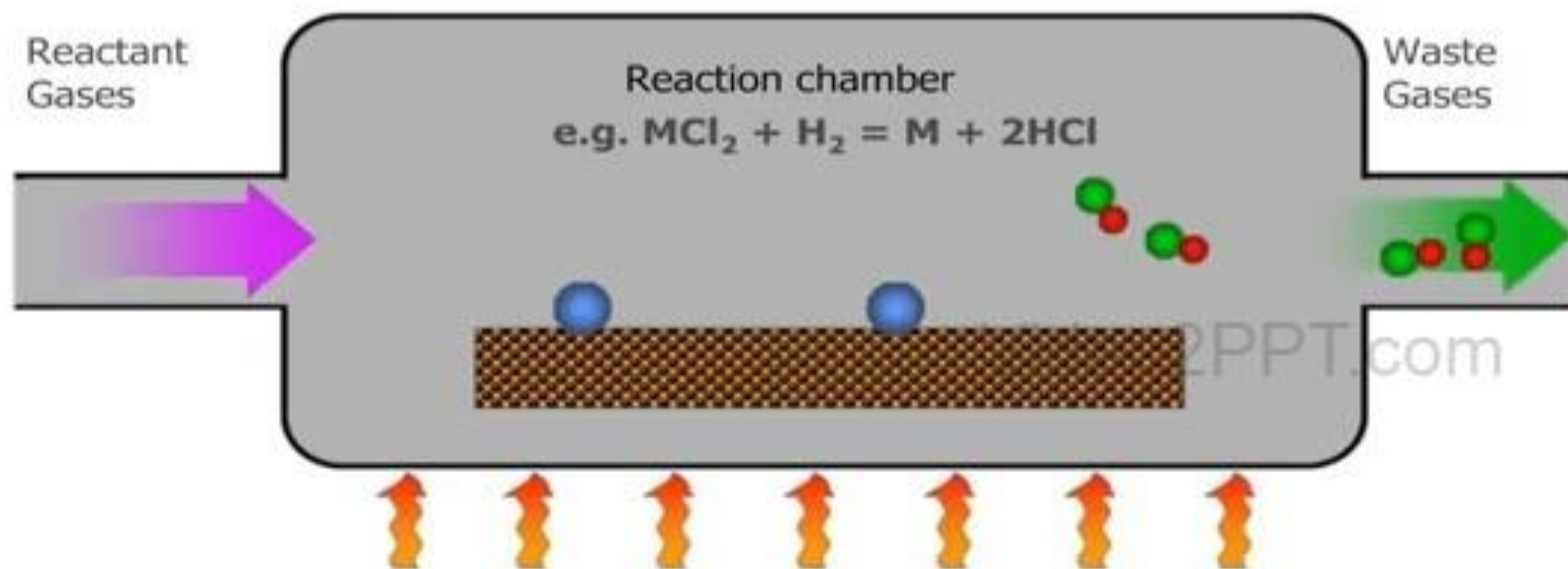


Chemical vapor deposition (CVD)

Chemical vapor deposition 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.

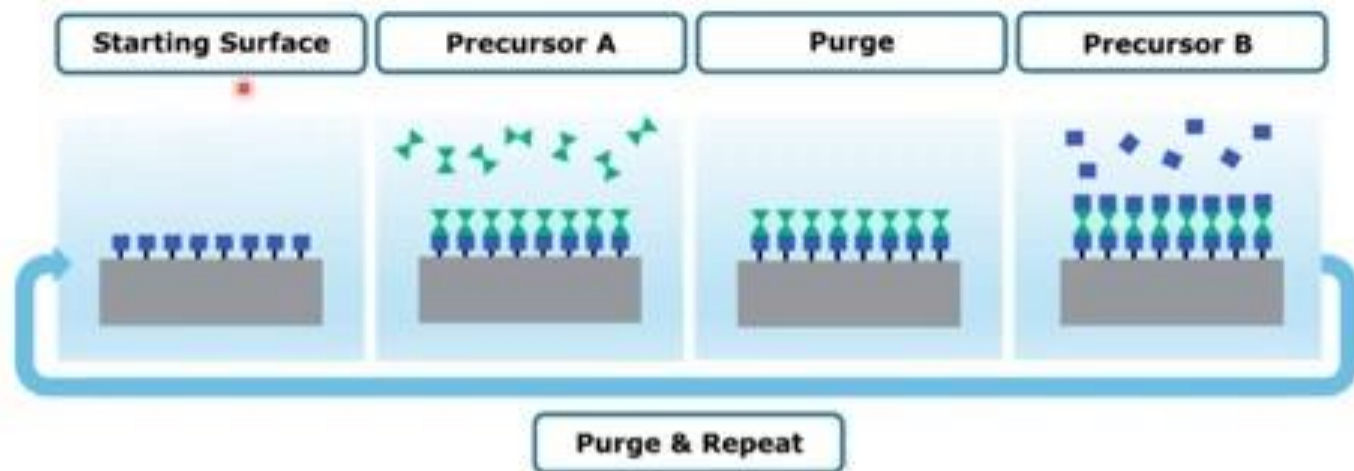
What is CVD?

"CVD is a process where gaseous precursors react to form a solid coating on a heated substrate"



Atomic Layer Deposition

- Atomic layer deposition (ALD) is a surface-controlled method for the deposition of films **from gas phase**.
- In ALD, the gaseous reactants are alternately pulsed to the substrates, and between the reactant pulses the reactor is purged with an inert gas.
- The film growth proceeds via self-limiting saturative surface reactions, which controls the film thickness and results in an excellent conformality and large area uniformity.
- The ALD has the advantage of precise thickness control at the Ångstrom or monolayer level.



ALD Process (SiO_2 Example)



PVD

Atoms as source material

Solid source materials

Vacuum/high vacuum

Elemental films mostly

Room temperature

Alloy films easily (W:N)

CVD & ALD

Molecules as source materials

Solid, liquid, gas precursors

Fluid dynamics important

Molecular/compound films mostly,
Chemical bonds broken & formed

Needs elevated temperatures
(or plasma activation)

Elements and compounds OK, alloys
more difficult

SUMMARY

- Various techniques are available for the synthesis of nanoparticles and nanostructured materials.
- The techniques available can be grouped broadly into the ‘top-down’ and ‘bottom-up’ approaches.
- These techniques can also be classified, based on the state of the matter from which the nanomaterials are synthesized.
- In bottom-up techniques, nanoparticles are prepared from the vapour or liquid phase, while in top-down approaches, they are made from solids.

Thanks for Watching