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R.V. COLLEGE OF ENGINEERING

(An Autonomous Institution affiliated to Visvesvaraya Technological University, Belagavi)

DEPARTMENT OF CHEMISTRY

Course: CHEMISTRY OF FUNCTIONAL MATERIALS

Course Code: 22CHY22C

Category: Professional Core Course

Semester: I/II (Stream: Electronics Engineering UG Branches)

UNIT-II: NANOMATERIALS AND THIN FILM FABRICATION TECHNIQUES

SYLLABUS

Nanomaterials and thin film fabrication techniques

Nanomaterials: Introduction, classification and properties. Synthesis- solution combustion, sol-gel method for thin films.

Carbon nanomaterials: Types, synthesis, properties, functionalization and applications of CNT and Graphene.

Thin film deposition techniques: Fabrication of thin films using CVD and PECVD and Metal organic chemical vapor deposition (MOCVD)-principle, fabrication and applications.

Abstract
The metal oxides and carbon materials find diverse applications ranging from photocatalysis to photovoltaics, mainly attributed to their admirable structure-electronic properties. In this regard, this module focuses on the device fabrication technologies of advanced functional materials through various chemical and physical methods. The correlation of preparation methods with materials properties could be easily tailored by understanding the precursor chemistry and the formation mechanism. The relation merits and demerits as well as the room for further development in the preparation method would be highlighted. Finally, the applications of the materials will be discussed.
Blow-up Syllabus

Sl No	Topic to be taught	Duration
1	Importance of nanomaterials and their advantage over bulk counterparts	1 hour
2	Different methods of preparation of nanomaterials and merit of chemical methods	1 hour
3	Sol-gel synthesis of nanomaterials and the reaction mechanisms	1 hour
4	Solution combustion synthesis and the association mechanisms	1 hour
5	Different forms of carbon materials and associated properties: Synthesis and applications of CNTs	1 hour
6	Graphene; properties, synthesis and applications	1 hour
7	Basis of thin film fabrication; CVD – preparation and mechanisms	1 hour
8	PECVD and MOCVD – preparation and mechanisms; similarities and differences among the deposition methods; applications	1 hour
9	Revision	

Nanomaterials are defined as materials with an average grain size less than 100 nanometers. The word "nano" originates from the Greek word "nanos" which means "dwarf". However, in scientific language it is a prefix which has a value equal to "one billionth, i.e. 10^{-9} ". Therefore, one nanometer is one billionth of a meter ($1 \text{ nm} = 10^{-9} \text{ m}$).

Examples:

1. Diameter of a hydrogen atom is about 0.1 nm. If ten hydrogen atoms are aligned in a line, then the resulting length would be approximately 1 nm. Similarly, 1 nm is approximately 5 silicon atoms aligned in a line.
2. A single strand of human hair is around 20,000 nm in diameter. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair.
3. Size of a DNA molecule is about 2.5 nm.

Properties of Nanomaterials

Nanomaterials have the structural features in between of atoms /molecules and the bulk materials. The properties of materials with nanometer dimensions are significantly different from those of atoms and bulk materials. This is mainly due to the nanoscale dimension of the materials which render them: (i) *large fraction of surface atoms* (ii) *high surface energy* (iii) *spatial confinement* and (iv) *reduced imperfections*, which do not exist in the corresponding bulk materials.

Due to their small dimensions, nanomaterials have extremely *large surface area to volume ratio*, which makes a large to be the surface or interfacial atoms, resulting in more “surface” dependent material properties.

Surface area:

As particle dimensions reduce towards the nanoscale, the surface-to-volume ratio proportionately increases. It further increases the surface active sites (reaction spots), which is the main reason for changing the properties of nanomaterial.

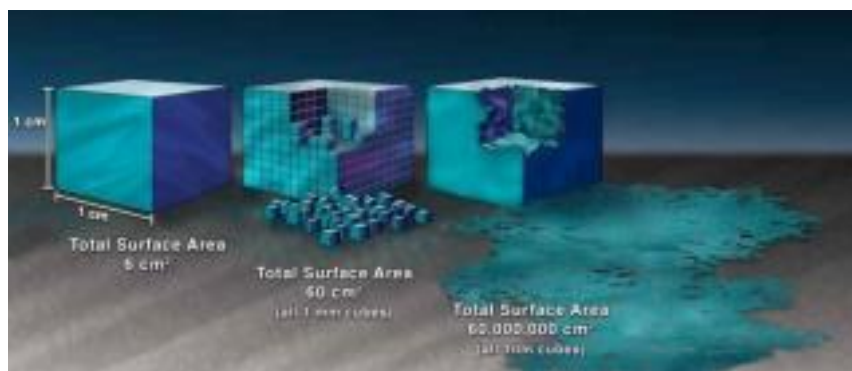


Fig. 1: Surface area variation from bulk to nano.

Optical properties of nanomaterials can be significantly different from their bulk counterpart. The change in optical properties is mainly due to the surface plasmon resonance and the increased energy level spacing. **Surface Plasmon Resonance (SPR):** The coherent excitation of entire free electrons in the conduction band may produce an in-phase oscillation, when the size of a metal nanocrystal is smaller than the wavelength of incident radiation, called surface Plasmon resonance. Thus, plasmon resonance depends on the particle size. In solid state physics, the plasmon represents the collective oscillation of a free charge in a metal, and may be considered as a kind of plasma wave. The positive electrical charge in the metal is fixed and the free electron is free to move around it. An applied external electric field, as from a light source, causes the free electrons at the surface of the metal to vibrate collectively, giving rise to surface plasmons. “Since electrons are also particles with an electric charge, when they vibrate they also generate an electric field, and when the electric field from the vibration of free electrons and the applied external electric field (e.g., electromagnetic waves) resonate the resulting phenomenon is referred to as a surface plasmon resonance” that takes place at the surface of the metal.

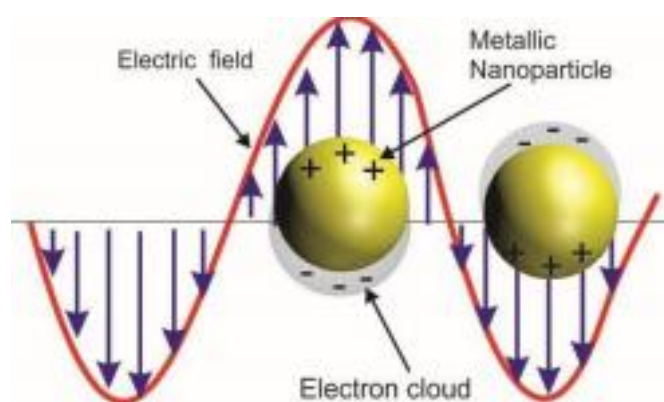


Fig. 2: SPR phenomena

For example, the wavelength of the SPR band maximum of a spherical Au nanoparticle is 520–550 nm. If a colloidal Au nanoparticle solution is now irradiated with visible light at these wavelengths (520–550 nm), the visible light corresponding to the green color is absorbed and the particles now display a red purple color, which is the complementary color to green. In a colloidal Ag nanoparticle solution which has a SPR band maximum near 400 nm, the blue color of the visible light is absorbed and the Ag particles now take on a yellow color, the complementary color to blue.



Fig. 3: Fluorescence emission of (a) Gold nanoparticles, and (b) Silver nanoparticles and of various sizes and absorbance

Catalytic Properties of Nanomaterials

Nanoscale catalysts have high specific surface area and surface energy, which ultimately lead to the high catalytic activity. Nano-catalyst improves the selectivity of the reactions by allowing reaction at a lower temperature, reducing occurrence of side reactions, higher recycling rates and recovery of energy consumption. Therefore, these are widely used in green chemistry, environmental remediation, efficient conversion of biomass, renewable energy development and other areas of interest.

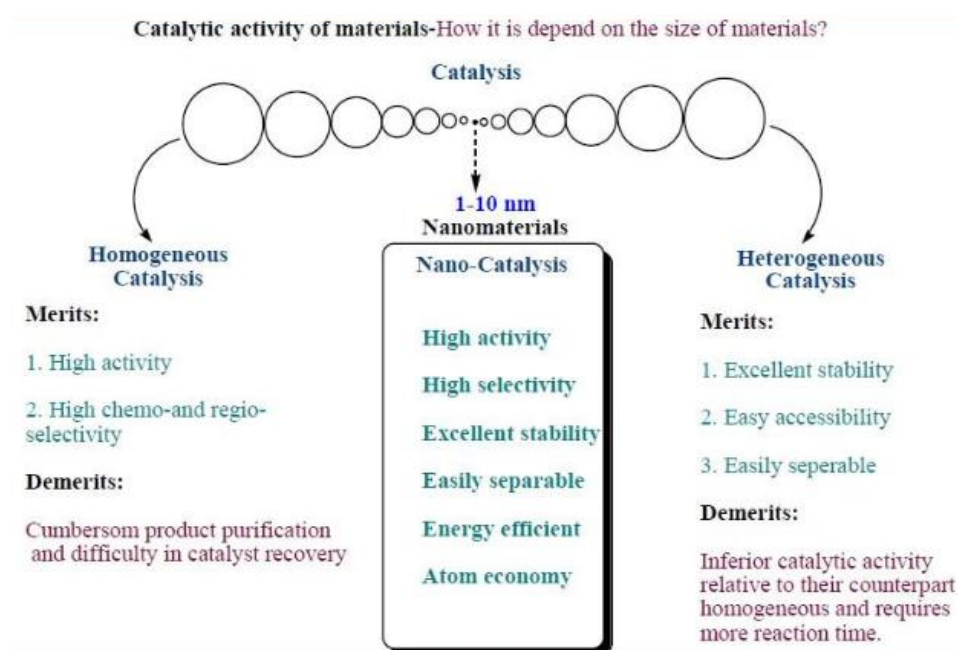
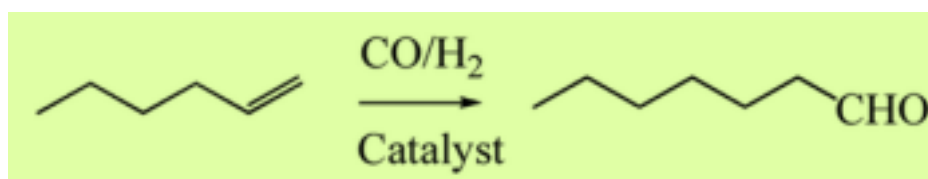


Fig. 4: Properties of Nano-catalyst

The rate of any chemical reaction depends on the number of active reaction sites on the catalyst. The surface

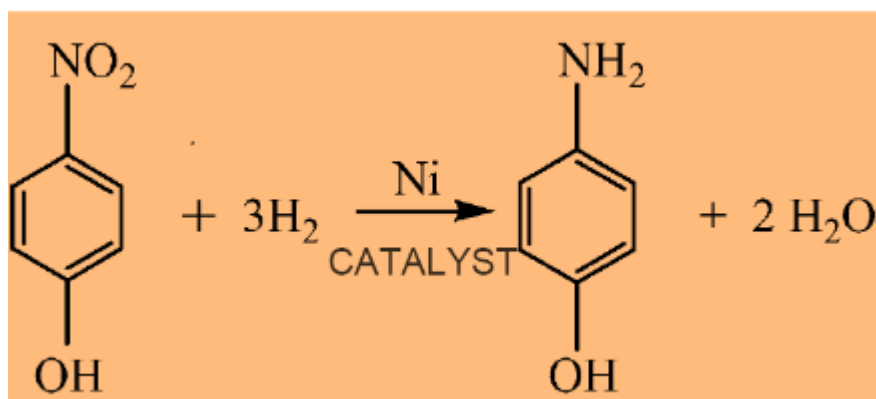
area of nanoscaled catalyst is larger than that of bulk material. As compared to bulk catalyst, the nanoscale catalyst of same material with same quantity has more number of active sites. Because of unsaturated valencies of surface atoms of Nanoparticle catalyst, they catalyze the reactions at much faster rates due to higher surface energies as compared to their respective bulk partners. Therefore, the nanoscaled material is found to exhibit very high catalytic efficiency than the corresponding bulk material.



Ex: 1. Hydroformylation of 1-Hexene over Rh/Nano -oxide

The highest activity with 100% total conversion and 96% yield of aldehydes was obtained with the Rh/nano ZnO catalyst. The Rh/nano-ZnO catalyst was found to be more stable and active than the corresponding rhodium catalyst supported on bulk ZnO (76% yield).

2. Catalytic hydrogenation of p-nitrophenol to p-aminophenol using nano-sized nickel



- The hydrogenation rate of nano-sized nickel is about 15 times higher than that of Raney Ni at similar reaction conditions
- The nano-sized nickel system suffers 54% deactivation, while the Raney nickel system suffers 80.4% deactivation only throughout six continuous hydrogenation cycles.
- These results indicate that the catalytic stability of nano-sized nickel system is superior to that of the Raney nickel system

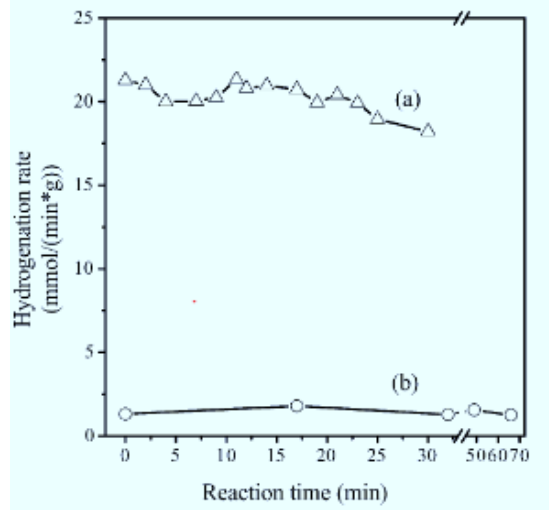


Fig. 5: Comparison of nano and bulk Ni catalyst property:

Classification of Nanomaterials

Nanostructured materials are classified as

1. **Zero dimensional (0D):** Nanomaterials are less than 100 nm in all three dimensions.
2. **One dimensional (1D):** Nanomaterials are less than 100 nm in any two dimensions.
3. **Two dimensional (2D):** Nanomaterials are less than 100 nm in any one dimensions, and
4. **Three dimensional (3D)** nanostructures: Nanomaterials are aggregations of any of the above (0, 1, 2D) dimensional nanomaterial with greater than 100nm in all the three above.

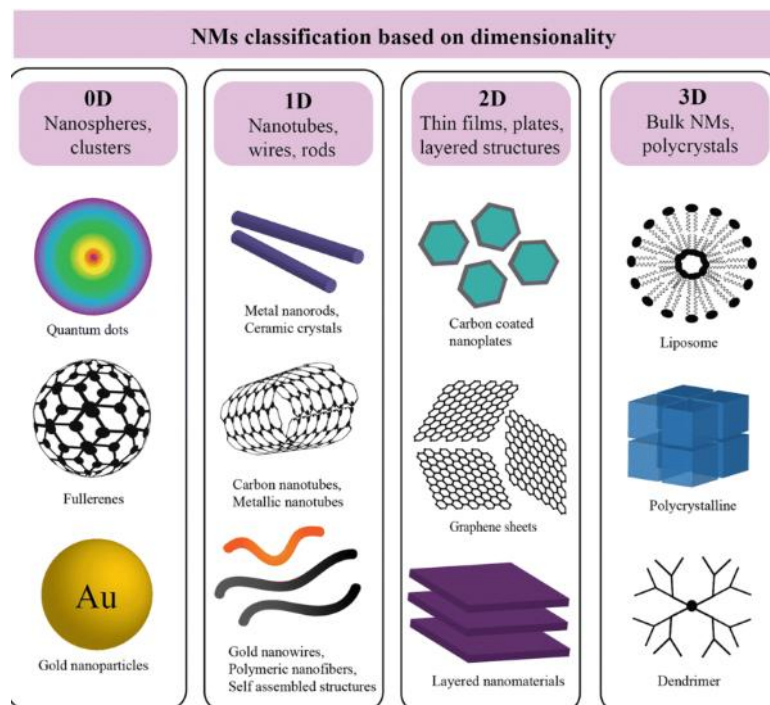
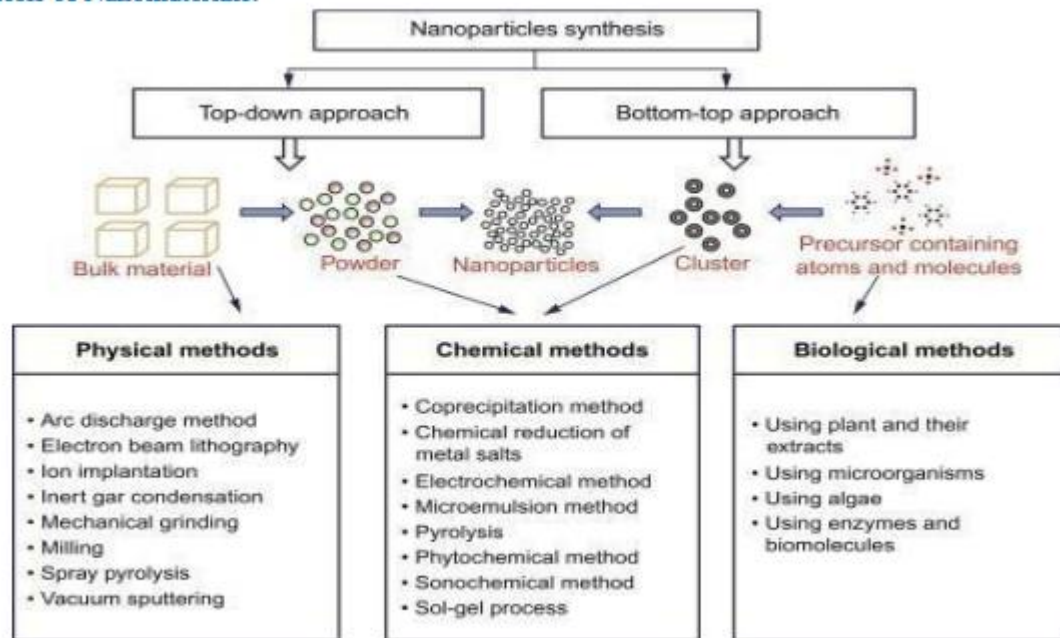


Fig.6: Examples for types of nanomaterials

Synthesis of Nanomaterials:



Top-Down approach

ADVANTAGES

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

DISADVANTAGES

Yields:

- 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

ADVANTAGES

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

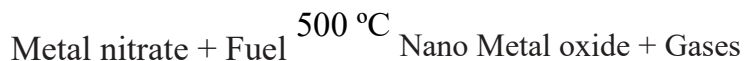
DISADVANTAGES

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

1. Low temperature solution combustion (SCS) method

Combustion method: is a low temperature, time saving, energy efficient, self propagating method, involving spontaneous exothermic redox reaction between metal nitrate and organic fuel, used to prepare nanomaterials.

Principle: The method is based on the utilization of heat energy produced during the exothermic spontaneous redox reaction between an oxidizer (metal nitrate) and a reducing agent (organic fuel). The oxidizer can be of any metal nitrates and reducing agents may be organic fuels, such as glycine, oxalic acid, urea, hexamine, sugar, EDTA, Detrose etc.



The amount of fuel can be calculated in such way that the total oxidizing valency of fuel should match with the total reducing valency of metal nitrate. The following formula can be used to calculate the amount of fuel:

For the calculation of valency of fuel and metal nitrate, the valency to be considered for the elements such as of N, O, H, C, and M^{n+} are 0, -2, +1, +4 and +n respectively.

Procedure:

Step1: Weighing and mixing of the reactants:



Weighing of all the reactants (metal nitrate and a fuel) according to stoichiometry, by using the above formula and dissolved in minimum quantity of distilled water in a beaker of suitable size.

The mixture is stirred on a magnetic stirrer till to get uniform solution as shown in figure (left side).

Magnetic stirrer on which uniform redox solution is obtained by stirring

Fig. 7: Magnetic stirrer

Step 2: Evaporation and combustion:

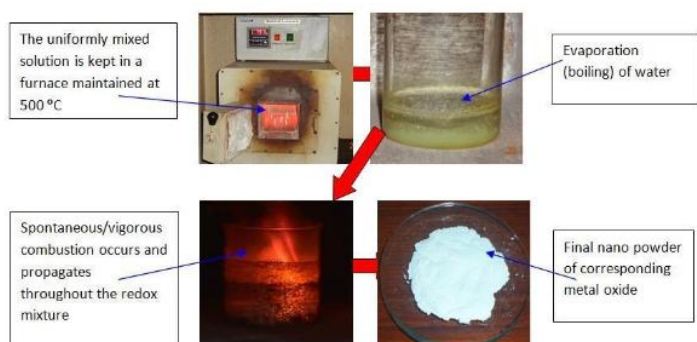


Fig. 8: Solution combustion syntheses steps

The clear solution is kept in a furnace (shown below) maintained at 500 °C. Firstly the solution undergoes evaporation that results in more concentrated, uniformly mixed viscous-gel type substance. After some time, the viscous-gel catches fire and propagates spontaneously in the redox mixture in the form of either a flame type or smouldering type. The combustion lasts for about 1-2 min. During the flame propagation large quantity of gasses and high temperature produced helps in the formation of respective nano metal oxide. The SCS has emerged as a viable technique for the preparation of advanced nano-metal oxide.

The most important advantages of SCS process are:

- (i) It is an easy and fast process that uses relatively simple equipment.
- (ii) High-purity products can be easily prepared by using this method.
- (iii) Composition, structure, homogeneity, size and stoichiometry of the products can be controlled.
- (iv) High exothermicity of the metal nitrate–fuel reaction permits incorporation of desired quantity of dopants in the various hosts of industrially useful phosphors.
- (v) This is the cheap method as compared to conventional solid state method.

Example: Synthesis of MgO by combustion method:

Chemicals: Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, (Mol. Wt=256.41) any organic fuel (say urea; NH_2CONH_2 ; Mol. Wt = 60) and distilled water.

Instruments/Glassware: High Temperature Furnace, 250ml Borosil glass beaker, Tong, Spatula, Weighing balance, Magnetic stirrer.

Calculation of fuel:

The valency of urea, $\text{N}_2\text{H}_4\text{CO} = 2(0) + 4(+1) + 1(+4) + 1(-2) = 6$

The valency of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = 1(+2) + 2(0) + 6(-2) + 6(0) = 10$

The amount of urea for 5.0 g of $\text{Mg}(\text{NO}_3)_2$ is calculated as follows.

$$\text{Wt of urea} = (5 \times 10 \times 60) / (256.41 \times 6) = 1.95\text{g}$$

Exercise:

- 1) ZnO from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Mol. Wt. =297.49) using glycine ($\text{NH}_2\text{CH}_2\text{COOH}$, Mol. Wt =75)
- 2) CaO from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Mol. Wt. =236.15) using glucose ($\text{C}_6\text{H}_{12}\text{O}_6$ = Mol. Wt =180)

Step 2: 'Sol' formation by hydrolysis: It involves the conversion of homogeneous solution into a “sol”. (A stable dispersion of colloidal particles of precursors in a solvent is known as sol) due to hydrolysis reaction. During hydrolysis, the alkoxide groups (-OR) are replaced via the nucleophilic attack of the oxygen atom of a water molecules, results in release of alcohol and formation of metal hydroxide (sol).

Step 3: 'Gel' formation by condensation

The colloidal solution is kept for aging. During aging condensation reaction between two metal hydroxyl/alkoxy species leads to M-O-M bonds with the release of H₂O/R-OH. This condensation process continues and finally results in a “gel”, an interconnected, a rigid and porous inorganic network covered completely with liquid phase. This transformation is called Sol-Gel transition.

Step 4: Drying of gel:

It involves removal of liquid phase from gel network. There are different ways of drying gel: (a) If the gel medium is dried, by removing the liquid solvent (under hyper critical conditions) without destroying the gel network, “aerogel” is produced.

(b) If the solvent is dehydrated by under ambient conditions (removal of R-OH groups), “xerogel” are produced.

(c) If the gel network is sintered at high temperature (800°C), densification, decomposition of gel results in complete collapse of gel net into powder.

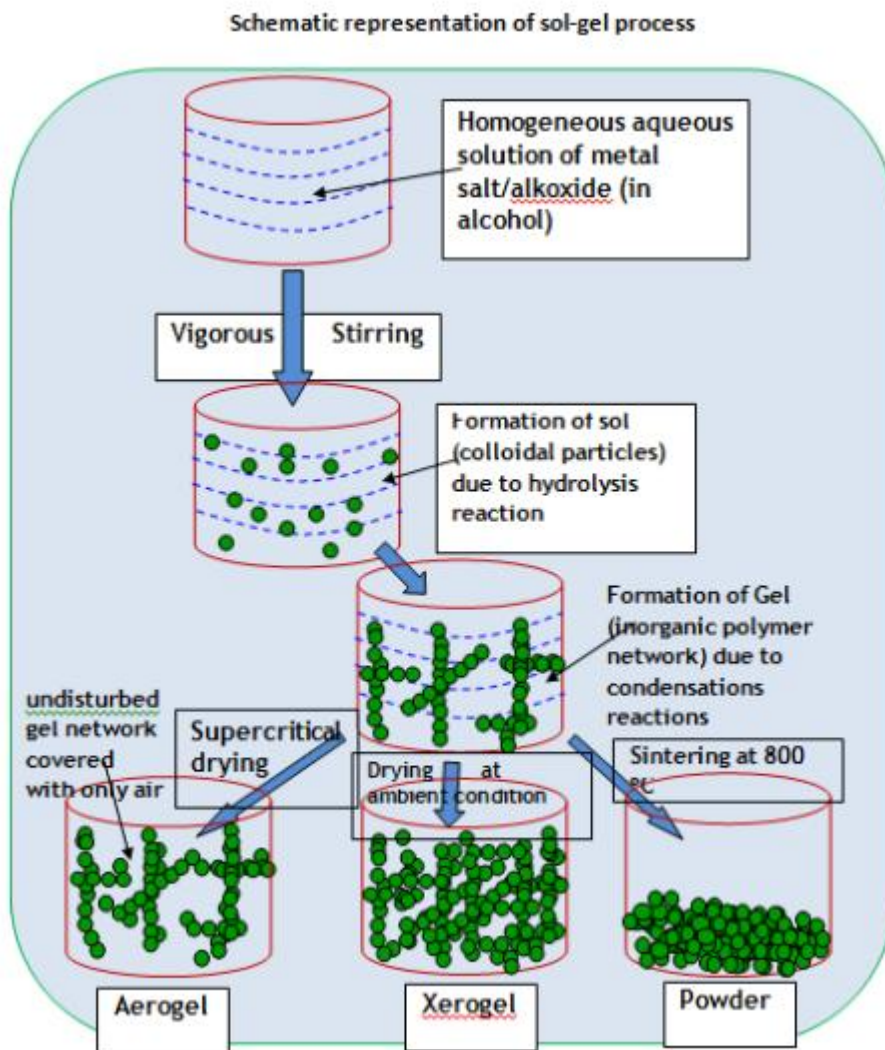


Fig. 9: Sol-gel synthesis flowchart

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*Example: Preparation of TiO<sub>2</sub> by Sol-gel method:*

Chemicals required: Titanium isopropoxide [Ti(O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>], absolute alcohol, distilled water, HNO<sub>3</sub>

Equipment/glassware: 250 ml glass beaker, magnetic stirrer, Furnace, oven.

Procedure: Stoichiometric quantity of titanium (IV) isopropoxide is dissolved in absolute ethanol and distilled water in the ratio of Ti:H<sub>2</sub>O=1:4. HNO<sub>3</sub> is added to adjust pH and restrain the hydrolysis process of the solution.

i) The solution is vigorously stirred for 30 min in order to form sol (a suspension of colloidal particle). ii) The sol is kept for aging for about 24 h. During aging sol is transformed into gel. (It is due to polycondensation and formation of inorganic network).

iii) In order to obtain TiO<sub>2</sub> nanoparticles, the gels are dried at 120 °C for 2 h to evaporate water and organic solvent. Then the dry gel is sintered at 450 °C for 2 h to obtain TiO<sub>2</sub> nanoparticles. Reaction mechanism:

Nucleophilic (H<sub>2</sub>O) attack on alkoxy group.

The advantages of this technique are:

1. It is a simple and economic technique, as the fabrication does not need expansive machinery or apparatuses.
2. It offers a high flexibility as one can produce materials with a wide range of stoichiometry and additional dopants.
3. It allows the fabrication of high quality coatings.
4. The starting materials are easily to obtain, not expensive and available in a high purity.
- 5.

Nanomaterials of variety of shapes can be prepared.

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Carbon Nanomaterials:

Carbon nanotubes are a new form of a hexagonal network of carbon atoms rolled up in the form of cylindrical shape.

Types of CNTs:

1. Single-Wall Nanotube (SWNT) (Arm Chair, Zig-Zag and Chiral)
 2. Multi-Walled Nanotubes (MWNT)
- Multiple rolled layers of graphene sheets

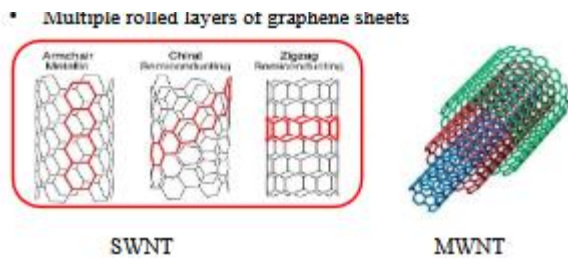


Fig. 10: Types of carbon nanotubes

Synthesis of CNTs by modified CVD method:

Chemical Vapor Deposition: Requirements:

- High Temperature Tubular furnace (500 to 1500 °C)
- Source of Carbon: Benzene, xylene, natural gas, acetylene
- Substrate: carbon, quartz, silicon
- Inert gas: Argon, Hydrogen, Nitrogen
- Catalyst: Ferrocene, Nickelocene, Cobaltocene

In this technique, carbon nano tubes grow from the decomposition of hydrocarbons at temperature range of 500 to 1200 °C in the inert atmosphere on the catalyst activated substrate.

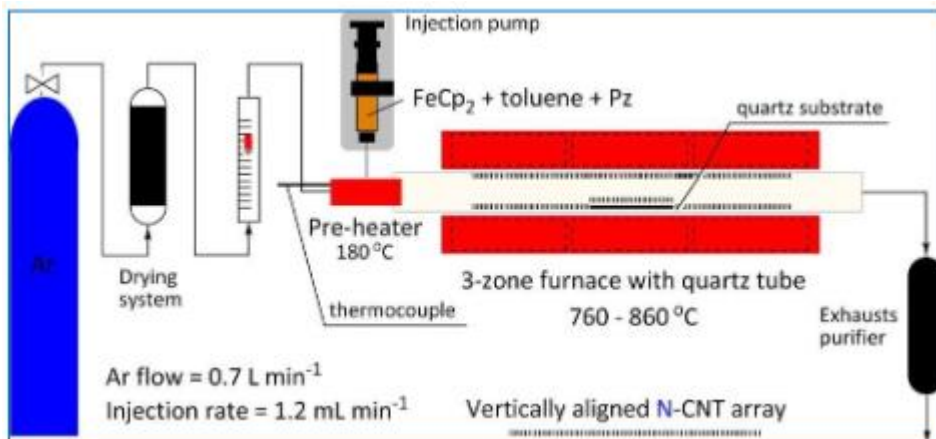


Fig. 11: CVD experimental set up

Working: The above figure shows the schematic diagram of a typical catalytic chemical vapor deposition system. It is equipped with a horizontal tubular furnace as the reactor. The tube is made of quartz, 30 mm in diameter and 1000 mm in length. Ferrocene and Benzene/toluene vapors acts as the catalyst (Fe) and carbon atom precursors respectively were transported either by argon, hydrogen or mixture of both into the reaction chamber, and decomposed into respective ions of Fe and carbon atoms, resulting into carbon nanostructures. The growth of the nanostructures occurred in either the heating zone, before or after the heating zone, which is normally operated between 500°C and 1150°C for about 30 min.

Mechanism of CNTs growth:

1. Diffusion of Hydrocarbon gas
2. Adsorption of Hydrocarbon gas on the surface active site of catalyst particles.
3. Dissociation (Homolytic fission) of Hydrocarbon in to highly reactive free radicals of 'C' and 'H'.
4. Repetition of steps 1, 2 and 3 leading to increase in concentration (saturation) of free radicals.
5. Precipitation (aggregation) of carbon free radicals results into crystal growth in the form tube on the surface. 'H' free radicals escape as H₂ gas.

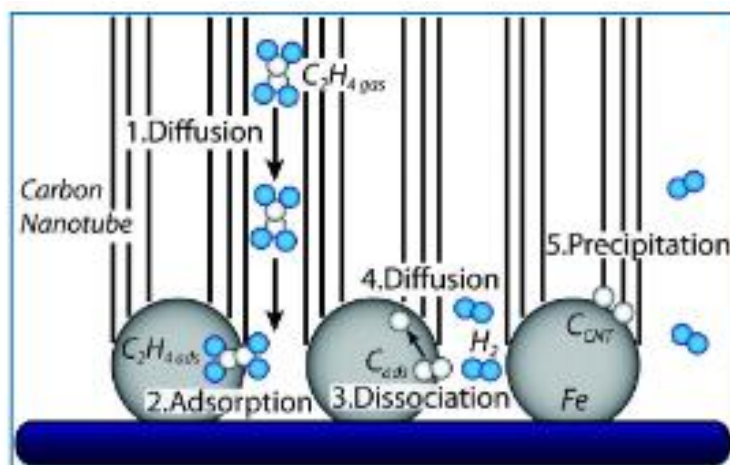


Fig. 12: Steps involved in CNTs growth

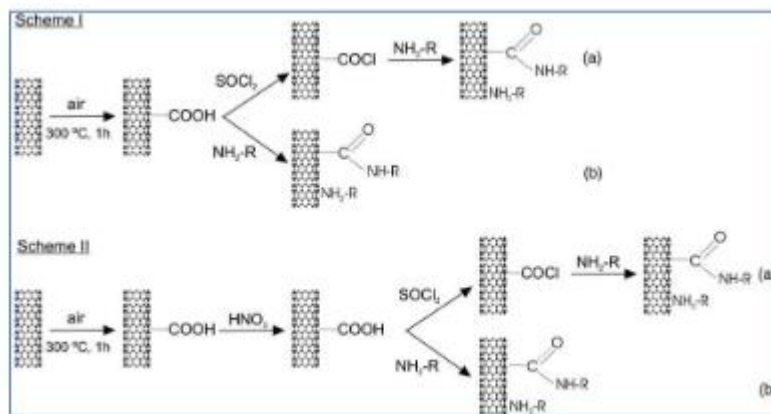
Functionalization of CNT:

CNTs may not have chemical affinity to the organic matrices and thus, the dispersion of CNTs into matrices is the biggest obstacle in practice. The modification/ functionalization of CNTs with other materials, makes it the most attractive and ultimate candidate for many applications which includes nanodevices, to organic electronics. The modification/ functionalization of CNTs can be simply divided into

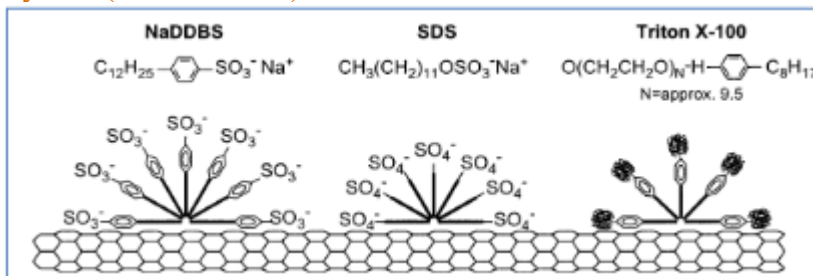
- Chemical (covalent) functionalization:** is based on the covalent bond of functional groups onto carbon form of CNTs. It can be performed at the end caps of nanotubes or at their sidewalls which have many defects. Direct covalent sidewall functionalization is associated with a change of hybridization from *sp*² to *sp*³ and a simultaneous loss of *p*- conjugation system.

b) Physical (Non-covalent) functionalization: It does not destroy the conjugated system of the CNTs sidewalls, and therefore it does not affect the final structural properties of the material. The CNTs are functionalized non-covalently by aromatic compounds, surfactants, and polymers, employing π - π stacking or hydrophobic interactions for the most part. In this approaches, the non-covalent modifications of CNTs can do much to preserve their desired properties, while improving their solubilities quite remarkably. (Ex: aromatic small molecule absorption, polymer wrapping, surfactants, biopolymers). Fig 12 : Types of CNT functionalization

Chemical (covalent) functionalization:



Physical (Non-covalent) functionalization:

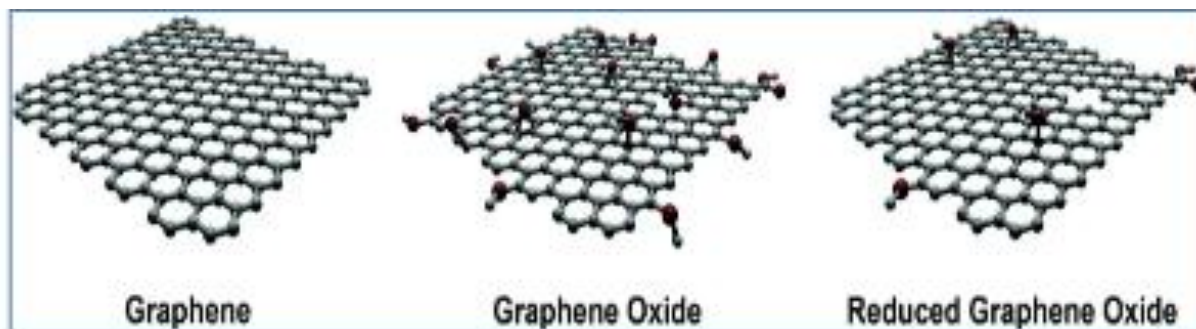


Applications of CNTs:

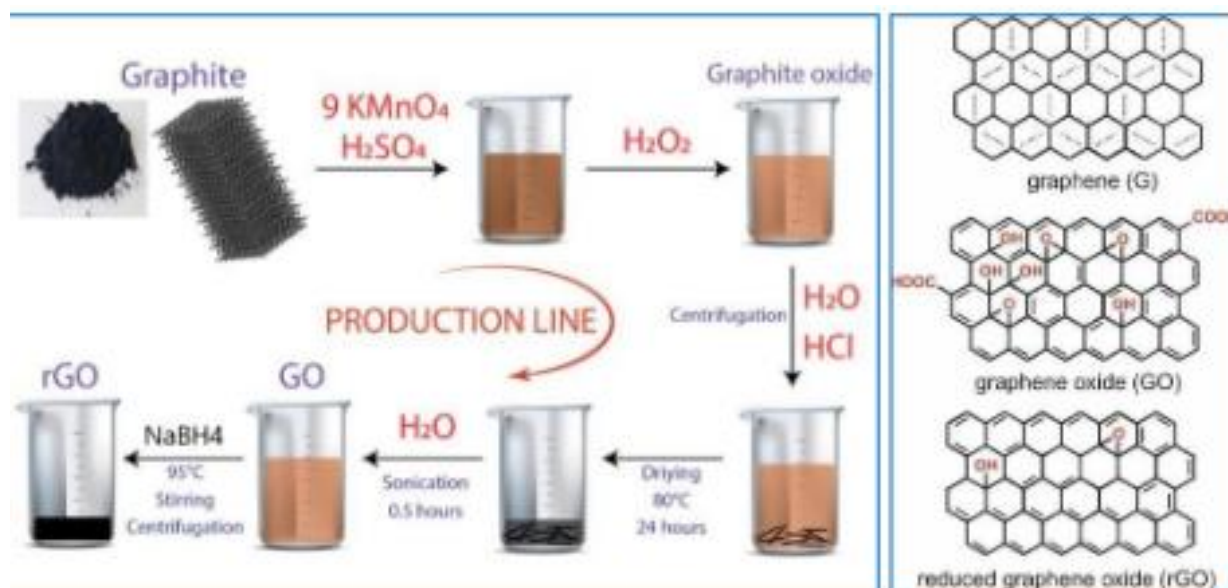
- Optoelectronic devices (Field Emission Display (FED))
- As *electrodes in batteries, capacitors and super capacitor electrodes.*
- As *electrode catalyst supports in Polymer Electrolyte Membrane (PEM) fuel cells •*
- *Hydrogen Storage material in hydrogen fuel car.*
- As electrically *powered artificial muscles.*
- Electro catalyst for water splitting, H₂ production.
- Adsorbent and photocatalyst for organic pollutants degradation.
- Sensor for heavy metal ion, gases, volatile organic compounds and biomolecules. •
- Drug carriers

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**Graphene:** Graphene is an allotrope of carbon made of a single layer of carbon atoms that are bonded together in a repeating pattern of hexagons. It is a purely carbon-based, honeycomb-structured, one-atom thick layer of carbon atoms (two dimensional sheet), bonded to one another by sp<sup>2</sup> hybridization.



**Synthesis of Graphene Oxide and Reduced Graphene Oxide-Modified Hummer's Method:** In a typical procedure, graphite (2 g) and NaNO<sub>3</sub> (2 g) were combined with H<sub>2</sub>SO<sub>4</sub> (90 ml) and stirred for 30 min in an ice bath. KMnO<sub>4</sub> (10 g) was added to the resulting solution, and the solution was then ultra sonicated at 50°C for 2 h. Deionized (DI) water (200 ml) and H<sub>2</sub>O<sub>2</sub> (12 ml, 35%) were then slowly added to the above solution, and the resulting solution was washed with HCl (300 ml, 10%). Additional washing with concentrated HCl (200 ml, 37%) followed by drying gives GO powder. The formed GO is further subjected to reduction by reacting with sodium borohydride.

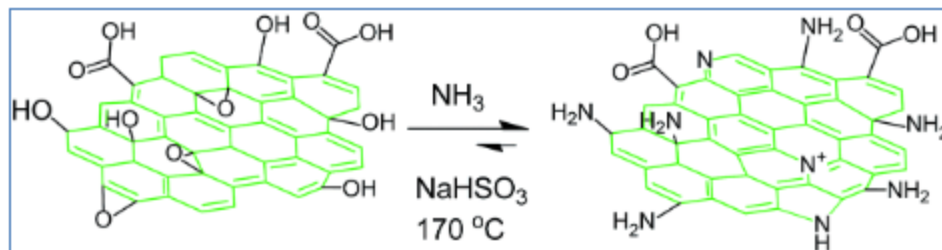


**Fig 13: Modified hummers method steps**

## Functionalization of Graphene

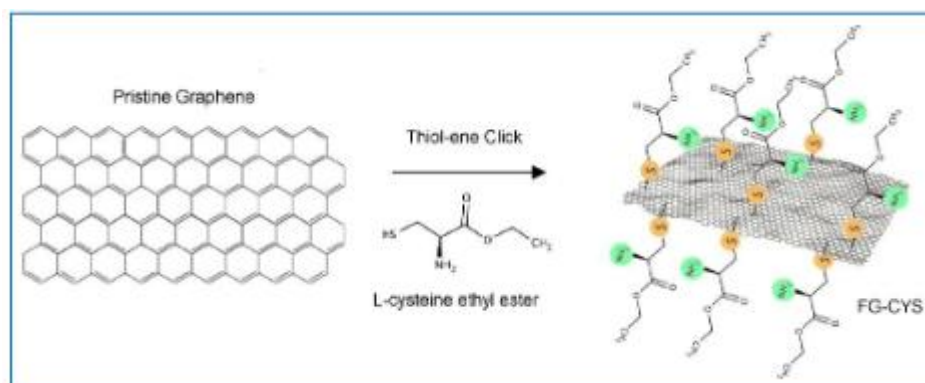
The functionalization is similar to CNT. It has two types (1) Covalent (chemical) and (2) Non-covalent (Physical) functionalization. The functionalization reduces the cohesive force between the graphene sheets and also to manipulate the physical and chemical properties.

The graphene oxide can be functionalized with amine group as follows. (Fig. 14)

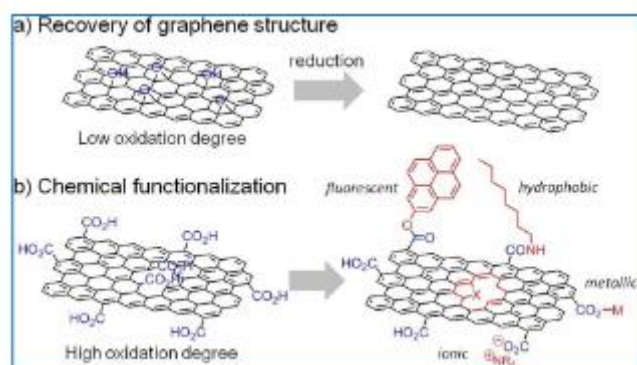


Ref: <https://doi.org/10.1039/C5CC08252H>

The graphene oxide can be functionalized with cysteine and thiolene group as follows (Fig. 15, 16).



Ref: <https://doi.org/10.3390/ma14112830>



Ref: <https://doi.org/10.1038/srep21715>

## Graphene Applications

Solar Cells, Batteries, Fuel cells, Medicine (Drug Delivery, Cancer Treatment, Gene Delivery, Photothermal Therapy, Diabetes Monitoring, Dialysis, Bone and Teeth Implantation, Tissue Engineering and Cell Therapy), UV Sensors, Biosensors, Transistors, Wearable Electronics, Flexible Screens, Optoelectronics, Optical Sensors, Water Purification, Desalination, Lubricants.

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## Thin film deposition techniques:

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications.

### CLASSIFICATION OF THIN FILMS

- (a) single crystals
- (b) epitaxial
- (c) polycrystalline
- (d) amorphous.

### PROPERTIES OF THIN FILMS

- (a) High surface to volume ratio
- (b) Geometrical control (dictated by substrate)
- (c) Compact
- (d) Single crystal like properties

### USES OF THIN FILMS

- Microelectronic devices
- Telecommunication devices
- Decorative coatings
- Optical coatings (windows, solar cells, etc.)
- Sensors
- Catalysts

Thin Film Deposition can be achieved through two methods: Physical Vapour Deposition (PVD) or Chemical Vapour Deposition (CVD)

CHEMICAL VAPOUR DEPOSITION CVD is the formation of a non-volatile solid film on a substrate by the reaction of vapor phase chemicals (reactants) that contain the required constituents. The reactant gases are introduced into a reaction chamber and are decomposed and reacted at a heated surface to form the thin film.

## CVD APPARATUS

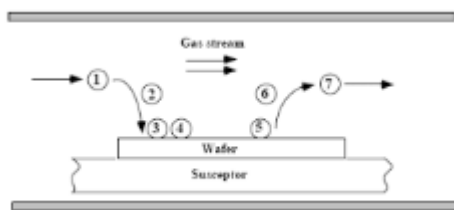
- Gas delivery system – For the supply of precursors to the reactor chamber
- Reactor chamber – Chamber within which deposition takes place
- Substrate loading mechanism – A system for introducing and removing substrates, mandrels etc •

Energy source – Provide the energy/heat that is required to get the precursors to react/decompose.

• Vacuum system – A system for removal of all other gaseous species other than those required for the reaction/deposition.

• Exhaust system– System for removal of volatile by- products from the reaction chamber. • Exhaust treatment systems – In some instances, exhaust gases may not be suitable for release into the atmosphere and may require treatment or conversion to safe/harmless compounds. • Process control equipment – Gauges, controls etc.. to monitor process parameters such as pressure, temperature and time. Alarms and safety devices would also be included in this category.

### Steps involved in a CVD process (Fig. 17)



1. Transport of reactants by forced convection to the deposition region.
2. Transport of reactants by diffusion from the main gas stream through the boundary layer to the wafer surface.
3. Adsorption of reactants on the wafer surface.
4. Surface processes, including chemical decomposition or reaction, surface migration to attachment sites (such as atomic-level ledges and kinks), site incorporation, and other surface reactions.
5. Desorption of byproducts from the surface.
6. Transport of byproducts by diffusion through the boundary layer and back to the main gas stream.
7. Transport of byproducts by forced convection away from the deposition region.

### Advantages:

- High growth rates possible
- Can deposit materials which are hard to evaporate
- Good reproducibility
- Can grow epitaxial films

### Disadvantages

- high temperatures ;
- complex processes ;
- toxic and corrosive gasses

## APPLICATIONS

Coatings

Such as wear resistance,

Corrosion resistance,

High temperature protection,

Erosion protection and

Combinations thereof.

Semiconductors and related devices –

Integrated circuits,

Sensors and

Optoelectronic devices

**Plasma-enhanced chemical vapor deposition (PECVD)** is a chemical vapor deposition process used to deposit thin films from a gas state (vapor) to a solid state on a substrate. Chemical reactions are involved in the process, which occur after creation of a plasma of the reacting gases. The plasma is generally created by radio frequency (RF) (alternating current (AC)) frequency or direct current (DC) discharge between two electrodes, the space between which is filled with the reacting gases.

The primary advantages of PECVD over conventional CVD are lower deposition temperatures, good conformity and step coverage on uneven surfaces, tighter control of the thin film process and high deposition rates.

While standard CVD temperatures are usually conducted in 600°C to 800°C, PECVD temperatures range from room temperature to 350°C, which enables successful applications in situations where the higher CVD temperatures could potentially damage the device or substrate being coated. By operating at a lower temperature, it creates less stress between thin film layers that have different thermal expansion/contraction coefficients. This allows for high-efficiency electrical performance and bonding to very high standards.

Because CVD is a diffusive gas driven process, it allows for better coverage on uneven surfaces such as trenches or walls with relatively high conformity. Alternatively, PVD coatings are a line-of-sight deposition and therefore can result in more variance in thin film depth if irregularities shield areas from coating. To a great extent, PECVD reduces the line-of-site issue for high conformity of thin films because the plasma stream can surround the substrate.

By varying the parameters of the plasma, excellent control of the material properties can be achieved including density and hardness, purity, roughness, or the refractive index of optical films. PECVD yields some of the fastest deposition rates while still maintaining high film quality.

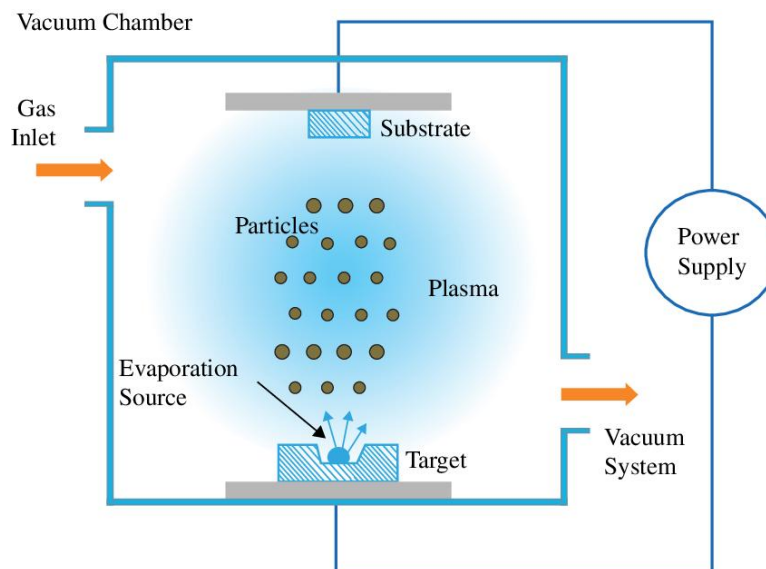
PECVD can produce unique compounds and films that cannot be created by common CVD techniques

alone, and produce films that demonstrate a very high solvent and corrosion resistance with chemical and thermal stability.

### How does Plasma Enhanced Chemical Vapor Deposition Work?

For typical semiconductor applications, the substrate is placed in the deposition chamber between two parallel electrodes — a grounded electrode and usually an RF-energized electrode. The substrate is heated in the range of 250°- 350°C.

Precursor gases such as silane ( $\text{SiH}_4$ ) and ammonia ( $\text{NH}_3$ ) are typically mixed with inert gases such as argon (Ar) or nitrogen ( $\text{N}_2$ ) to control processes. These gases are introduced into the chamber via a shower head fixture over the substrate that helps to spread the gas more evenly onto the substrate. The plasma is ignited by electrical discharge (100 – 300 eV) between the electrodes, creating a glowing sheath around the substrate that contributes to thermal energy driving the chemical reactions. These reactions first occur in the plasma as a result of precursor gas molecules colliding with highly energized electrons which then, via gas flow, travel to the substrate where they react and are absorbed on the substrate surface to grow films. The chemical by-products are then desorbed and pumped away, completing the deposition process. Higher gas flow rates can yield higher deposition rates, which along with operating temperatures, control properties such as thickness, hardness or refractive index.



**Fig. 18: Reactor design for PVD**



## Metal-Organic Chemical Vapour Deposition.

MOCVD is a technique that used to grow/deposit thin solid films, usually semiconductors, on solid substrates (wafers) using organo metallic compounds as sources.

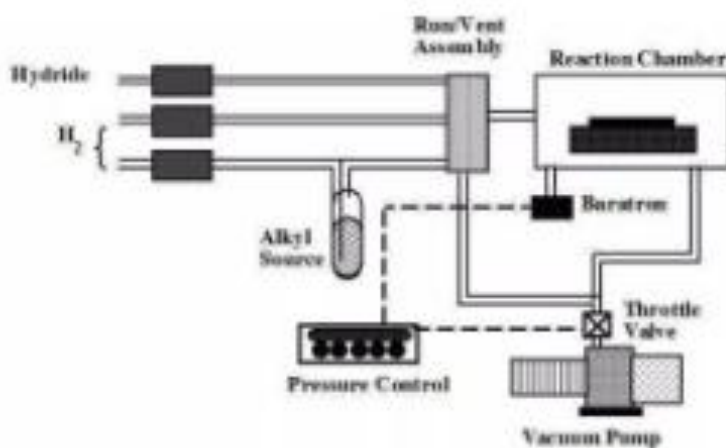
The films grown by MOCVD are mainly used for the fabrication of electronic and optoelectronic devices.

The electronic and optoelectronic devices produced by MOCVD are used in cell phones , optical communication, optical storage (CD, DVD), traffic lights, bill boards (LEDs), lighting and solar cells. Using MOCVD we can build up many layers, each of a precisely controlled thickness, to create a material which has specific optical and electrical properties.

Principle of operation: transport of precursor molecules (group-III metalorganics + group-V hydrides or alkyls) by a carrier gas ( $H_2$ ,  $N_2$ ) onto a heated substrate; surface chemical reactions.

Main parts of MOCVD System (Fig. 19)

### Main parts of MOCVD System



1. Source Supply System: The different sources which are used are shown in Fig.

- TMI (Trimethylindium) and TEG (Triethylgalium) are used as source material for In and Ga respectively.
- $NH_3$  is used as a source material for nitrogen.
- $N_2$  is used as a carrier gas to bring TMI and TEG into the reactor.
- $H_2$  gas is used for the thermal treatment of the substrate.
- Reactive gases are fed in to the reactor through the mass flow controllers (MFC)

2. Reaction Chamber/ Reactor:

Epitaxial vapor growth is made inside the reactor at different conditions (temperature, pressure, gas flow).

