

## CHAPTER- I

### INTRODUCTION TO NANOMATERIALS

Introduction: Nanomaterials: Definition - Classification based on dimensions - Size dependent properties. Types of nanomaterials: Nanoparticles: Synthesis by chemical reduction method. Nanoporous materials: Synthesis by sol-gel method. Nanowires: Synthesis by VLS mechanism. Carbon Nanotubes (CNTs): Single walled and multi walled nanotubes - Mechanical and electrical properties of CNTs - Applications of CNTs - Synthesis of CNTs by electric arc discharge method and laser ablation method.

#### 1.1 INTRODUCTION

Nano science and technology is a broad and interdisciplinary area growing explosively worldwide in the past few years. Nanomaterials are cornerstones of nanoscience and nanotechnology. Now a days in research & development the major sectors are energy, environment, water technology, pharmaceuticals etc. The usage of nanomaterials are enormous as energy storage devices such as fuel cells, detection of threats in defense, navy, drug delivery and water purification. Industrial revolution has made life easy and pleasant. Today's high speed personal computers and mobile communications would not have certainly been possible without the use of nano science and nano technology.

#### 1.2 MAIN TERMINOLOGY

- a) **Nano science and nanotechnology** - The science and technology which deals with the particles in size between 1 to 100nm is known as nano science and nano technology.
- b) **Classification of nanomaterials on the basis of dimensions**

On the basis of reduction in size of materials in different dimensions, nanomaterials are classified into three groups.

S. No.	Reduction in size in different coordinates	Size	Examples
1.	3-dimensions	< 100 nm	Nanoparticles, quantum dots
2.	2-dimensions	< 100 nm	Nanotubes, nanowires, nanofibers
3.	1-dimension	< 100 nm	Thin films, coatings

- c) **Classification based on pore dimensions**

A useful way to classify nanoporous materials is by the diameter size of their pores, since most of the properties, which are interesting for the applications of adsorption and diffusion are dependent on this parameter. The prefix nano- means a typical dimension between 1 and 100 nm. In this range material properties change drastically, when materials interact with other molecules. In fact, pore diameter establishes the size of molecules that could diffuse inside and comparison between the pore size and the dimension of guest molecule gives an idea about diffusion and interaction properties. If the two dimensions are same, we can expect that the molecule-wall interaction will be prevalent along with the molecule-molecule interaction. By the other way, if guest molecules are smaller than the pore size, there will be less molecule wall

interaction than the molecule-molecule interaction during the diffusion process.

According to IUPAC definition, nanoporous materials are classified in three main groups depending on their pore dimension:

**Microporous materials ( $d < 2$  nm):** These materials have very narrow pores. They can host only small molecules, such as gases or linear molecules, and generally show slow diffusion kinetics and high interaction properties. They are generally used in gas purification systems, membrane filters or gas-storage materials.

**Example:** Na-Y and naturally occurring clay materials.

**Mesoporous materials ( $2 < d < 50$  nm):** These materials have pores with diameter size enough to host some big molecules, for example aromatic systems or large polymeric monomers. Diffusion kinetics of the adsorbed molecules is often due to capillarity, with an initial interaction with the pore wall followed by pore filling. These systems can be used as nano-reactors for the polymerization or adsorbing systems for liquids or vapours.

**Example:** MCM-41, MCM48, SBA15 and carbon mesoporous materials etc.

**Macroporous systems ( $d > 50$  nm):** Pores of these materials could host very large molecules, such as poly-aromatic systems or small biological molecules, and interactions with pore walls are often secondary respect to the interactions with other molecules, overall in the case of very small guest molecules. These materials are principally used as matrices to store functional molecules, as scaffolds to graft functional groups, such as catalytic centres, and as sensing materials, thanks to the quick diffusion of chemical species in the pore system.

**Example:** Carbon micro tubes, Porous gels and porous glasses

#### d) **Synthetic approaches for nanomaterials**

- (i) **Bottom-up approach:** The building of nanostructures starting with small components such as atoms or molecules is called bottom-up approach.

Ex: Chemical vapour deposition, Sol-Gel Process, Chemical Reduction methods, etc.

- (ii) **Top-down approach:** The process of making nanostructures starting with larger structures and breaking away to nano size is called top-down approach.

Ex: Lithography, Ball milling, Epitaxy, etc.

- e) **Porosity** – It is the ratio of pore volume to its total volume. Here, pore volume is the difference between the total volume and solid volume.

- f) **Pore diameter** - The average or effective diameter of the openings in a membrane, screen, or other porous material is known as pore diameter. Based on the pore diameter range, porous materials are classified into three types.

- (i) **Microporous materials:** They are materials having the average pore diameter less than

2nm Ex: Zeolites, organic frame works and surgical tape.

(ii) Mesoporous materials: They are materials having the average pore diameter in the range of 2nm to 50 nm Ex: Mobile Crystalline Materials (MCM-41), Mesoporous Molecular Sieves, Xerogels, Silica, Alumina, titanium Oxide and Niobium oxide materials.

(iii) Macroporous materials: They are materials having the average pore diameter greater than 50nm. Ex: Porous glasses and Aerogels.

- g) **Wafer** - A wafer is a thin slice of semiconductor or substrate material.
- h) **Sol** - It is a colloidal suspension of very small solid particles in liquid medium. Ex: Ink and Blood.
- i) **Gel** - It is a colloidal suspension of very small liquid particles in solid medium Ex: agar, gelatin, jelly and tooth paste.
- j) **Aerogel** - It is a synthetic porous ultra light material derived from a gel, in which the liquid component of the gel has been replaced with a gas. Ex: Silica aerogel, Alumina aerogel and carbon aerogel. Silica aerogel is a best insulator as well as lowest density solid. It porosity is 99%, surface area is 1000 m<sup>2</sup>/gm, Its average pore size is 2-50nm.
- k) **Xerogel** - A solid formed from a gel by drying with unhindered shrinkage is called a xerogel.
- l) **Surface area** - The accessible or detectable area of solid surface per unit mass of material is called the surface area.
- m) Characterization techniques of nanomaterials

S. No.	Techniques	Information acquired
1.	Scanning Electron Microscopy (SEM) with Energy-dispersive X-ray spectroscopy	Surface topography (up to 10nm) and composition
2.	Transmission Electron Microscopy (TEM)	Surface morphology (up to 0.2nm)
3.	Atomic Force Microscopy	Identification of individual surface atoms
4.	Particle Size Analyzer	Particle Size distribution
5.	FT-Raman Spectra	Distinguish single walled carbon nanotubes and multi walled carbon nanotubes
6.	Photoluminescence Spectra	CNT chirality or Asymmetry determination
7.	X-ray photoelectron spectroscopy	Electronic state of the element

- n) **Chiral** - A chiral molecule is a type of molecule that has non-superimposable mirror images (i.e. enantiomers).

Example: A carbon having four different substituents.

- o) **Helicity** - It is a form of axial chirality or with respect to axis non-superimposable mirror images. Example: Protein folding.

### 1.3 SIZE DEPENDENT PROPERTIES OF NANOMATERIALS

The various properties, which get tremendously altered due to the size reduction in at least one dimension are:

- Chemical properties: Reactivity; Catalysis.
- Thermal property: Melting point temperature.
- Electronic properties: Electrical conduction.
- Optical properties: Absorption and scattering of light.
- Magnetic properties: Magnetization.

#### 1.3.1 Chemical Properties

- Based on the surface area to volume effect, nanoscale materials have:
  - Increased total surface area.
  - Increased number of atoms accessible on the surface.
  - Increased catalytic activity of those large number surface atoms.
  - Different/tunable surface catalytic properties by the change in shape, size and composition.
- Hence, nanoscale catalysts can increase the rate, selectivity and efficiency of various chemical reactions.

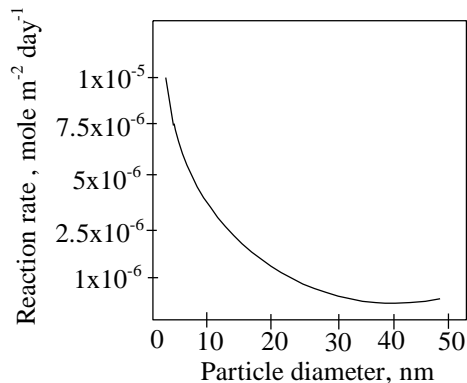
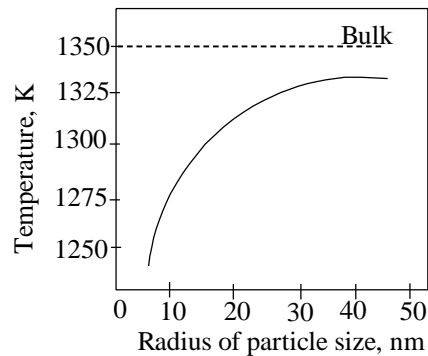


Fig 1.1: Effect of Particle Size on the Reaction Rate

#### 1.3.2 Thermal Properties

- The melting point of a material directly correlates with the bond strength. In bulk materials, the surface to volume ratio is small and hence the surface effects can be neglected. However, in nanomaterials the melting temperature is size dependent and it decreases with the decrease particle size diameters.
- The reason is that in nanoscale materials, surface atoms are not bonded in direction normal to the surface plane and hence the surface atoms will have more freedom to move.



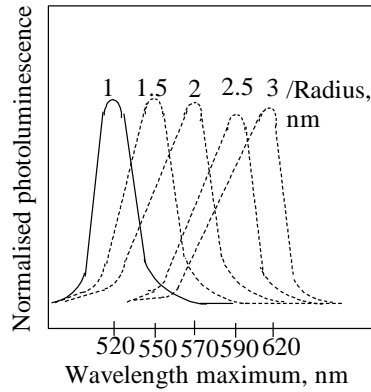
**Fig 1.2: Effect of Particle Size on the Melting Point**

### 1.3.3 Electronic Properties

- In bulk materials, conduction of electrons is delocalized, that is, electrons can move freely in all directions.
- When the scale is reduced to nanoscale, the quantum effect dominates. For zero dimensional nanomaterials, all the dimensions are at the nanoscale and hence the electrons are confined in 3-D space. Therefore no electron delocalization (freedom to move) occurs.
- For one dimensional nanomaterials, electrons confinement occurs in 2-D space and hence electron delocalization takes place along the axis of nanotubes/nanorods/nanowires.
- Due to electron confinement, the energy bands are replaced by discrete energy states which make the conducting materials to behave like either semiconductors or insulators.

### 1.3.4 Optical Properties

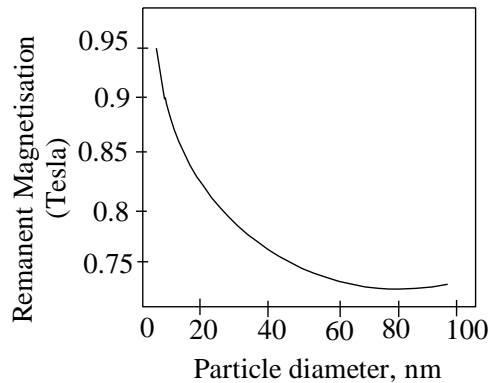
Because of the quantum confinement in nanomaterials, the emission of visible light can be tuned by varying the nanoscale dimensions. It is observed that the size reduction in nanomaterials shifts the emission of peak towards the shorter wavelength (blue shift).



**Fig. 1.3: Effect of particle size on photoluminescence**

### 1.3.5 Magnetic Properties

- The size of magnetic nanoparticles also influences the value magnetization. The figure 5.4 illustrates the effect of particle size on the saturation magnetization of zinc ferrite. The magnetization increases significantly below a grain size of 20nm. Hence, by decreasing the particle size of a granular magnetic material it is possible to improve the quality of magnets fabricated from it.



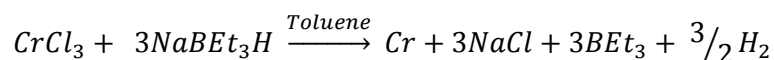
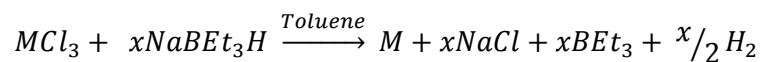
**Fig 1.4: Effect of Particle Size on the Saturation Magnetization**

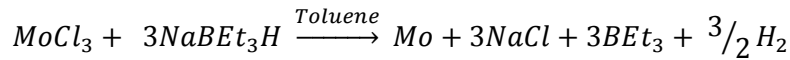
## 1.4 NANOPARTICLES

Particles or powders with particle size less than 100nm are called nanoparticles.

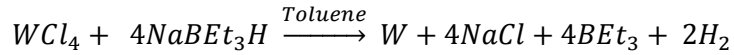
### 1.4.1 Synthesis of Nanoparticles by Chemical Reduction Method

Group VIB metal halides like  $\text{CrCl}_3$ ,  $\text{MoCl}_3$ ,  $\text{WCl}_4$  can be reduced into their corresponding metals by using  $\text{NaBEt}_3\text{H}$  (sodium triethoxy boron hydride) with toluene as the solvent at room temperature.





When  $M = W$ , then  $x = 4$ ,



#### 1.4.2 Properties of Nanoparticles

- (i) As the particle size decreases, surface area increases. This enhances the catalytic activity of the nanoparticles.
- (ii) Reduction of particle size from micron to nanometer scale influences their optical properties.

For Example: CdS in micron size appear as red, 6nm size appear orange in colour, 4nm size is yellow coloured and 2nm size appear as white.

- (iii) Reduction of particle size from micron to nanometer scale influences the thermal properties like melting point and thermal conductivity.

#### 1.4.3 Applications of Nanoparticles

- a) Silver nanoparticles have good antibacterial properties, and are used in surgical instruments, refrigerators, air-conditioners, water purifiers etc.
- b) Gold nanoparticles are used in catalytic synthesis of silicon nano wires, sensors carrying the drugs and in the detection of tumors.
- c) ZnO nanoparticles are used in electronics, ultraviolet (UV) light emitters, piezoelectric devices and chemical sensors.
- d) TiO<sub>2</sub> nanoparticles are used as photocatalyst and sunscreen cosmetics (UV blocking pigment).
- e) Antimony-Tin-Oxide (ATO), Indium-Tin-Oxide (ITO) nanoparticles are used in car windows, liquid crystal displays and in solar cell preparations.

### 1.5 NANOWIRES

Nanowires are cylindrical solid wires structures with one of the dimensions smaller than 100 nm and length few micrometers. Nanowires are quantum mechanically one dimensional structures when their diameter is comparable to the electron's de Broglie wavelength in the plane perpendicular to the growth direction.

One dimensional confinement of electrons in nanowires causes the change in density of states and allowed energy levels in nanowires. Quantum confinement in nanowires also allows the

study of other unique phenomena such as ballistic transport, coulomb blockade and phonon confinement. One interesting phenomena observed in nanowires is that we can easily play with the band gap which is an important parameter in fabricating devices for specific applications. Since the bandgap increases with the decrease of nanowire diameter, nanowire can emit visible light with high efficiency. Nanowire bandgap is also affected by the surface chemistry because of the high surface area to volume ratio. Depending on the passivant on the nanowire surface the bandgap can also be increased or decreased accordingly.

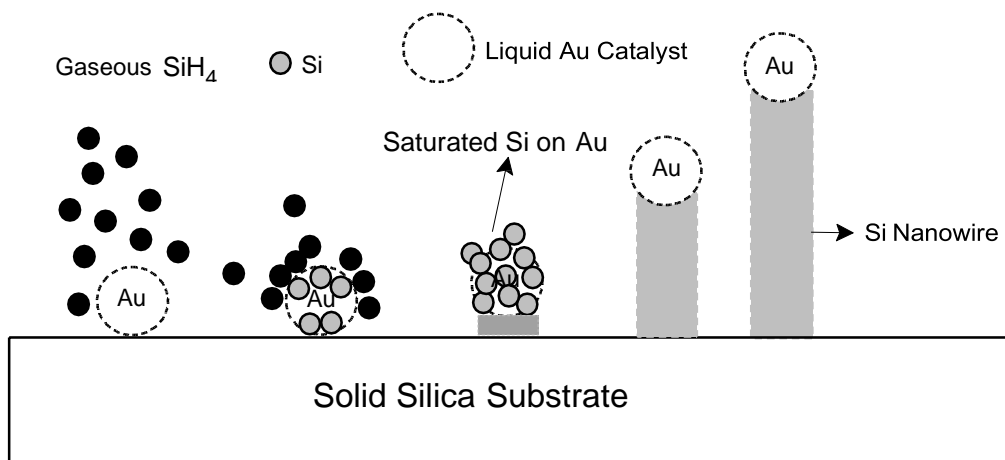
A well accepted mechanism for the growth of nanowires through gas phase reaction is vapour-liquid-solid process. To grow any nanowire, the material used must be soluble in the catalyst nanoparticles. For example to grow silicon nanowire gold nanoparticles are used because silicon vapour is soluble in gold nanoparticles. To grow gallium nitride nanowire iron nanoparticles are used because the reactants gallium and nitrogen are soluble in iron nanoparticles.

### 1.5.1 Synthesis of Silicon nanowires (Vapour-Liquid-Solid Mechanism)

The **vapour-liquid-solid** mechanism was proposed in 1964 as an explanation for silicon whisker growth from the gas phase in the presence of a liquid gold droplet placed upon a silicon substrate. The VLS is a mechanism for the growth of one-dimensional structures such as nanowires. The growth of a crystal through direct adsorption of a gas phase on to a solid surface is generally very slow. The VLS mechanism circumvents this by introducing a catalytic liquid alloy phase which can rapidly adsorb a vapor to supersaturation levels and from which crystal growth can subsequently occur from nucleated seeds at the liquid-solid interface. The physical characteristics of nanowires grown in this manner depend, in a controllable way, upon the size and physical properties of the liquid alloy.

It follows two step processes

- In the first step, diffusion of vapour phase ( $\text{SiH}_4$  reactants) takes place into the gold liquid phase (catalyst nanoparticles).
- In the second step, supersaturation of Si reactants occur in the gold liquid phase which causes the precipitation of Si solid phase (nanowire).



**Fig.1.5: Vapour-Liquid-Solid Mechanism of Si nanowires**



Figure 1.5 shows the Vapour-Liquid-Solid Mechanism of Si nanowires. The substrate is first covered with a coating of gold nanoparticles and heated to a temperature in a furnace so that it becomes liquid. Simultaneously the precursor Silane ( $\text{SiH}_4$ ) is introduced into the furnace where it vapourises to form silicon vapour. During the reaction, silicon vapour diffuses and dissolves in the molten gold nanoparticles. When the concentration of silicon reaches supersaturation level, the excess material (silicon) precipitates and grows as nanowires.

The catalyst for the VLS mechanism must follow the following conditions

- The catalyst must be inert (non-reacting) to the reaction products (during synthesis).
- The solid solubility of the catalyzing agent is low in the solid and liquid phases of the substrate material.
- It must form a liquid solution with the crystalline material to be grown at the nanowire growth temperature.

### 1.5.2 Applications of Nanowires

- a) Nanowires are used in electron devices like field effect transistors, light emitting diodes, bio sensors, optical switches, solar cells and photo detectors.
- b) Nanowires replace copper in computers and in electronics.
- c) Self-assembled nanowires (NWs) have strong flexibility of tailoring their chemistry which makes them the building blocks for the nano-sized devices, e.g. in communication systems by miniaturization of light sources and development of nanotechnologies and biosensors.
- d) Vapor-Liquid-Solid (VLS) is a typical growth mechanism applied for nanowires growth in which metal is normally used as catalyst.

## 1.6 NANOPOROUS MATERIALS

Nanoporous materials are all about holes that are all less than 100 nm. Like many nanostructured materials nanoporous materials abound in the natural world. The petroleum industry has been using naturally nanoporous materials called zeolites as catalyst for decades, though the majorities now used are synthetic. Activated carbon is an example of a nanoporous material that like zeolites has been in use for a long time.

### 1.6.1 Synthesis of Nanoporous materials by Sol-gel process

#### Sol-Gel Process:

“Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid”.

#### Precursors

The precursor used in sol-gel process for the synthesis of nanoporous materials are metal alkoxides  $\text{M}(\text{OR})_4$ . They readily react with water to form gels.

Examples

- Tetra methoxy silane [ $\text{Si}(\text{O}_3\text{CH}_3)_4$ ]
- Tetra ethoxy silane [ $\text{Si}(\text{O}_2\text{C}_2\text{H}_5)_4$ ]
- Tetra butoxy titanate [ $\text{Ti}(\text{O}_4\text{C}_4\text{H}_9)_4$ ]

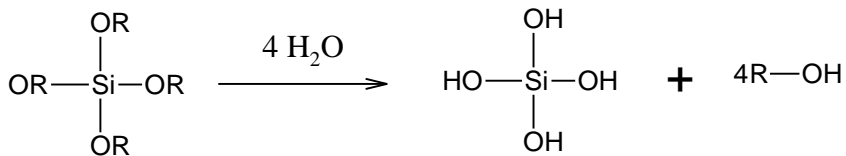
**Process (Synthesis of silica aerogel)**

This process consists of four main steps.

1. Hydrolysis of precursors
2. Condensation followed by polycondensation
3. Gelation
4. Supercritical drying

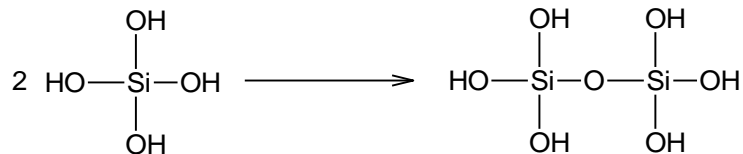
**1. Hydrolysis**

It occurs by the addition of water to any one of the precursor material to form silanol (Si-OH) particles.



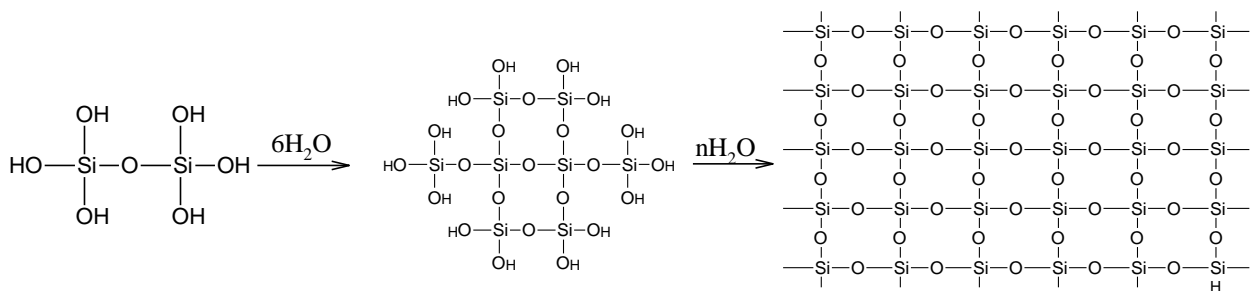
**2. Condensation**

The self condensation of silanol groups produces siloxane linkages filled with by products of water and alcohol.



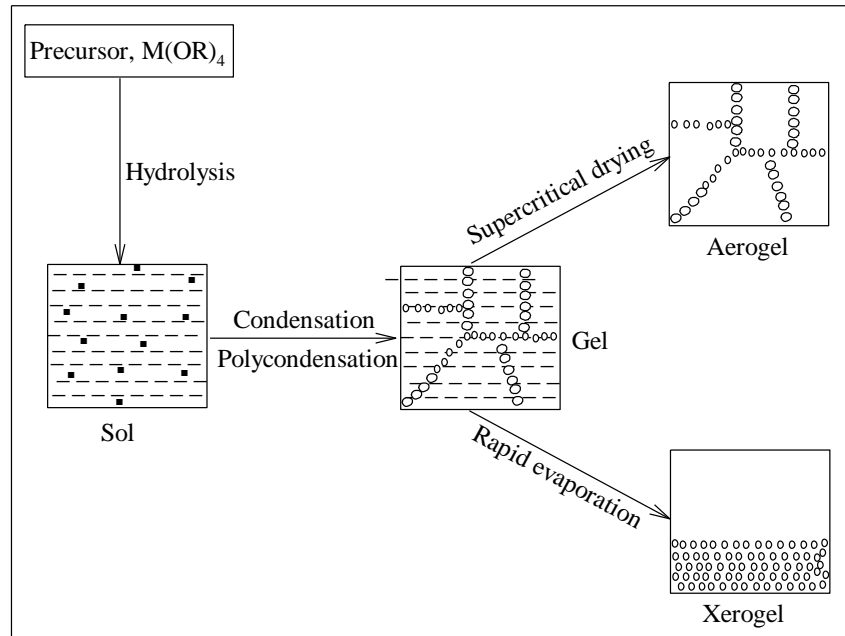
**3. Polycondensation**

The condensation process continues to form poly condensed silica gel with Si-O-Si linkages.



**4. Drying**

The gels are subjected to super critical drying in an autoclave. The critical pressure and critical temperature used are 78 bar and 294°C respectively in order to remove liquid from silica gel to form the network structure of silica aerogel.



**Fig. 1.6: Sol-gel process**

### 1.6.2 Advantages of Sol-gel process

- It produces thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.
- It produces thick coating to provide corrosion protection performance.
- It easily shapes materials into complex geometries in a gel state.
- It has low temperature sintering capability, usually 200-600°C.
- It provides a simple, economic and effective method to produce high quality coatings.

### 1.6.3 Applications of Sol-gel process

- It can be used in ceramics manufacturing processes as an investment casting material or as a means of producing very thin films of metal oxides for various purposes.
- Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio) sensors, medicine (e.g. controlled drug release) and separation (e.g. chromatography) technology.
- One of the more important applications of sol-gel processing is to carry out zeolite synthesis.

- Other elements (metals, metal oxides) can be easily incorporated into the final product and the silicalite sol formed by this method is very stable.
- Other products fabricated with this process include various ceramic membranes for microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

#### 1.6.4 Properties and applications of Nanoporous materials

- Nanoporous materials consist of a regular organic or inorganic framework supporting a porous structure.
- Typical examples of nanoporous solids are zeolites, activated carbon, metal–organic frameworks, ceramics, silicates, aerogels, pillared materials, various polymers and inorganic porous hybrid materials.
- Nanoporous materials are separated into three subtypes: microporous materials ( $\leq 2$  nm), mesoporous materials (2–50 nm) and macroporous materials ( $> 50$  nm).
- In recent years, nanoporous materials have been recognized as promising candidates for the multifunctional applications such as catalysis, ion-exchange, gas storage, low density magnetic storage, etc.
- In addition nanoporous materials are also of scientific and technological importance because of their ability to absorb and cooperate with atoms, ions and molecules on their sizeable interior surfaces and pore space.
- Nanoporous materials have the surface area of  $500\text{-}1000\text{m}^2/\text{gm}$ , which enhances the catalytic activity.
- Since they have very low thermal conductivity values, they are used in thermal insulators.
- Because of high porosity (90-99%), they are extensively used in membrane technology.
- They are of lightweight materials (density:  $0.003\text{-}0.8$  gm/cc)

### 1.7 SYNTHESIS OF NANOMATERIALS BY CHEMICAL VAPOUR DEPOSITION (CVD)

#### 1.7.1 Principle

Chemical vapour deposition (CVD) method involves a transport of reactant gases towards the substrate kept at some temperature where reactants crack into different products which diffuse on the surface and undergo certain chemical reactions at appropriate site nucleate and grow to form desired films, coatings, wires and tubes.

#### Precursors

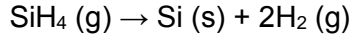
The common precursors used in CVD reactions are

- Metal hydrides –  $\text{SiH}_4$  ,  $\text{GeH}_4$
- Metal halides-  $\text{TiCl}_4$  ,  $\text{TaCl}_5$  ,  $\text{WF}_6$
- Metal organics-  $\text{AlMe}_3$  ,  $\text{AlBu}_3$  ,  $\text{Fe}(\text{CO})_5$  ,  $\text{Ni}(\text{CO})_4$

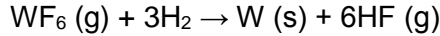
#### CVD Reactions

(i) Thermal Decomposition (Pyrolysis):

Silicon deposition from  $\text{SiH}_4$  at  $650^\circ\text{C}$

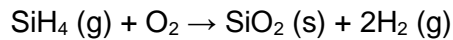


(ii) Reduction: W-deposition at  $300^\circ\text{C}$



(iii) Oxidation:

$\text{SiO}_2$  deposition at  $450^\circ\text{C}$



### Types of CVD

In CVD, the temperature of  $300\text{--}1200^\circ\text{C}$  is usually used. The heat input can be in the form of thermal, light, plasma and so on. This give rise to number of CVD techniques.

S. No.	Name of the CVD	Source of thermal energy
1.	Thermal activated CVD	IR radiation, RF heating
2.	Photo assisted CVD	Arc lamps, CO laser, Nd:YAG laser, Argon ion laser
3.	Plasma assisted CVD	RF diode, microwave
4.	Metal organic CVD	It uses organo metallic as precursors

### Mechanism

The system follows a five step mechanism for any type of CVD.

- Transport of precursors into the reactors
- Absorption and diffusion of precursors on the substrate
- Chemical reactions at the substrate
- Deposition and growth of film
- Transport of unreacted precursors and by-products

### 1.7.2 Advantages

- Versatile- CVD can deposit any element or compound.
- CVD produces high dense films.
- Economical in production since many products can be coated at a time.
- Used for coatings or freestanding structures
- Fabricates net or near-net complex shapes
- Self-cleaning—extremely high purity deposits ( $>99.995\%$  purity)
- Conforms homogeneously to contours of substrate surface
- Controllable thickness and morphology

- i) Forms alloys
- j) Coats internal passages with high length-to-diameter ratios
- k) Simultaneously coat multiple components
- l) Coats powders

### 1.7.3 Applications

- a) CVD can be used for the synthesis of nanotubes and nanowires.
- b) CVD can be used for hard coatings and metal films which are used in microelectronics.
- c) CVD can also be used for preparing semiconducting devices, dielectrics, energy conversion devices etc.
- d) CVD processes are used on a surprisingly wide range of industrial components from aircraft and land gas turbine blades, timing chain pins for the automotive industry, radiant grills for gas cookers and items of chemical plant to resist various attacks by carbon, oxygen and sulphur.
- e) Surface modification to prevent or promote adhesion.
- f) Photoresist adhesion for semiconductor wafers Silane/substrate adhesion for microarrays (DNA, gene, protein, antibody, tissue).
- g) BioMEMS and biosensor coating to reduce "drift" in device performance.
- h) Promote biocompatibility between natural and synthetic materials Copper capping Anti-corrosive coating

## 1.8 PHYSICAL VAPOUR DEPOSITION

Nanomaterials in the form of thin films, multilayer films, nanoparticles and nanotubes can be produced by physical vapour deposition methods.

### Definition

Physical vapour deposition (PVD) is a technique by which a metal, ceramic or a compound can be converted into gaseous form and then deposited on the surface of a substrate.

In general, PVD methods are subdivided into:

1. Evaporation
2. Sputtering
3. Pulsed Laser Deposition or Laser Ablation

### EVAPORATION

The source materials used in this process are generally refractory metals such as W, Ta, Mo etc. In evaporation technique, both substrate and source materials (to be deposited) are placed inside the vacuum chamber ( $10^{-6}$  to  $10^{-7}$  torr). The vacuum is required to allow the molecules to evaporate and to move freely in the chamber. An electron gun (e-gun) is used to produce electron beam of 10 keV. This beam is directed at the source material in order to develop sufficient vapour so as to produce deposits on wafer or substrates. Figure.1.7 shows the schematic diagram of evaporation equipment.

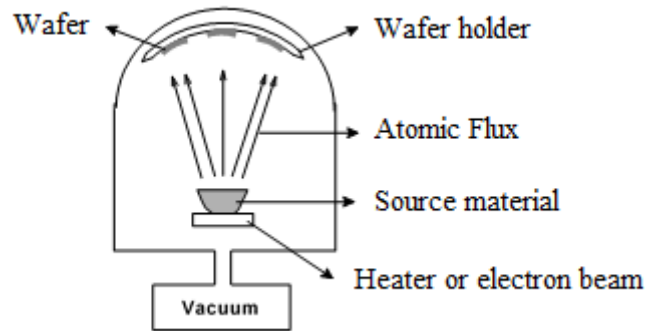


Fig. 1.7 Schematic diagram of evaporation equipment

## SPUTTERING

The source materials used in this process are generally an alloy, ceramic or a compound. In sputtering technique, a high energy atom in ionized form usually  $\text{Ar}^+$  is used to hit the surface atoms of the targeted source material. Then the knocked out atoms in vapour form are deposited on the surface of the substrate to produce a uniform coatings.

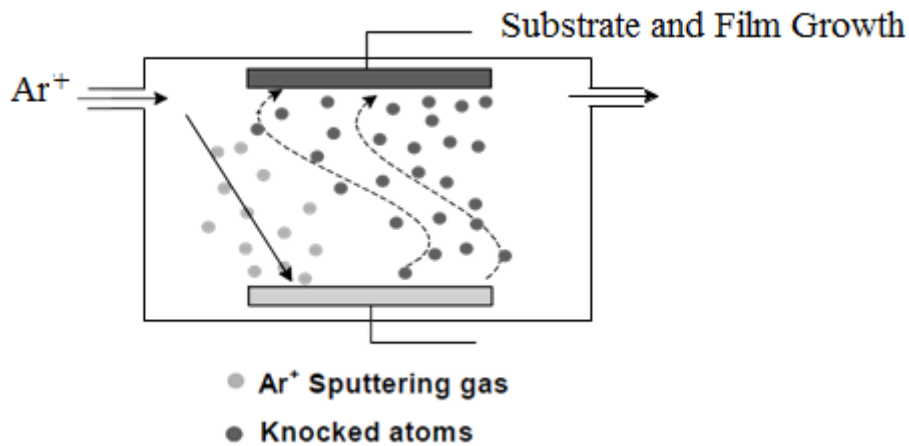
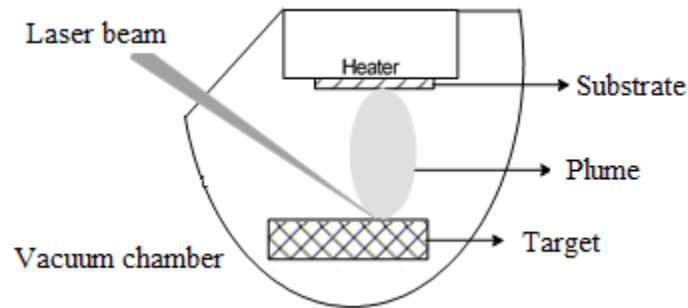


Fig. 1.8: Schematic diagram of sputtering equipment

## Pulsed Laser Deposition or Laser Ablation

Pulsed Laser Deposition (PLD) is a thin film deposition technique that is used to deposit materials on substrates. A base system consists of a target, substrate carrier which is mounted in a vacuum chamber. An excimer laser is used to energize the surface of a target to produce a deposition plume. The plume is typically directed towards the substrate where a thin-film is deposited. Since each shot of the laser is directly related to the amount of material ablated, the deposition rate can be calibrated and controlled very precisely. Figure.1.9 shows the schematic diagram of pulsed laser deposition.



**Fig.1.9: Schematic diagram of Pulsed Laser Deposition**

### Advantages

- Ultrapure films or particles can be produced by PVD since it uses a vacuum environment.
- PVD can provide good structural control by careful monitoring of the processing conditions.
- Materials can be deposited with improved properties compared to the substrate material.
- Almost any type of inorganic material can be used as well as some kinds of organic materials.
- The process is more environmentally friendly than processes such as electroplating.

### Disadvantages

- Since PVD operates in a low pressure range, it increases the complexity of deposition and cost of production.
- It is a line of sight technique meaning that it is extremely difficult to coat undercuts and similar surface features.
- High capital cost.
- Some processes operate at high vacuums and temperatures requiring skilled operators.
- Processes requiring large amounts of heat require appropriate cooling systems.
- The rate of coating deposition is usually quite slow.

### Applications

- PVD is used to produce the deposit of various metals, alloys or compounds in the form of coatings or films for:

Optics (Ex: Antireflection coatings)

Electronics (Ex: Metal contacts)

Mechanics (Ex: hard coatings on tools) etc.

- PVD coatings are generally used to improve hardness, wear resistance and oxidation resistance.
- PVD coatings use in a wide range of applications such as:

Aerospace



Automotive  
Surgical/Medical  
Dies and moulds for all manner of material processing  
Cutting tools  
Fire arms 3030

## 1.9 APPLICATIONS OF NANOMATERIALS

Nowadays in many aspects of our lives more and more materials with new properties are required to ensure further development of mankind. The appearance of nanomaterials has given a great impulse to further discoveries in various fields of science.

Nanomaterials with attractive electronic, optical, magnetic, thermal and catalytic properties have attracted great attention due to their widespread applications in physics, chemistry, biology, medicine, material science and interdisciplinary fields.

Some basic distinctive properties of nanomaterials are a very small particle size, the large surface area, accelerating the interaction between nanomaterials and the environment in which they are placed as well as the absence of point defects resulting in strength of nanomaterials ten times the strength of steel. These properties explain the fact that even a gram of a nanomaterial may be more effective than a large number of ordinary matters. Today nanomaterials have been used in such areas as:

- Production technologies
- Military engineering
- Nuclear power engineering
- Electronic equipment
- Protection of materials surface
- Medicine and biotechnology

### **Production technologies:**

- It is important and perspective now to use nanomaterials in composites as components of various functions.
- In the production of steels and alloys adding nanopowders helps to reduce porosity and improve the range of mechanical properties.
- Manifestation of superplasticity in nanostructured aluminum and titanium alloys makes their use promising in the manufacture of complex shapes details and for using as a connecting layer in welding different solid state materials.
- Very large specific surface nanopowders promote their use in a number of chemical processes as catalysts.

### **Military engineering:**

- Ultra-fine powders are used in a number of radar absorbing coatings for aircraft, created with the use of technology "Stealth", and promising types of explosives and incendiary.
- Carbon nanofibers are used in special ammunition intended for the scrapping of the enemy power systems (so-called "graphite bomb").

### **Nuclear power engineering:**

The beginning of nuclear power engineering was given by the ultra-fine powders. These powders are commonly used in industrial processes for the separation of uranium isotopes. Prospects for

the development of nuclear energy by bringing the particles to the nanostate are mainly associated with a decrease in the average consumption of natural uranium. This happens mostly at the expense of increasing the depth of the nuclear fuel combustion. To do this, scientists are exploring the possibility of the creation of coarse-grained structures of nuclear materials, which can be porous. These nanomaterials will promote a high retention of fission products.

**Material surface protection:**

In some cases, for reliable operation, it is necessary to ensure the high water and oil repellency properties of material surface. Some examples of such products may be car windows, glass planes and ships, protective clothing, wall storage tanks for liquids, building construction, etc. At present the titanium oxide nanoparticles coating with sizes of 20-50 nm and a polymer binder have been developed. This coating greatly reduces the wettability of the surface with water, oil and alcohol solutions.

**Medicine and biotechnology:**

A number of areas in which nanotechnology is used successfully are as follows:

**1. Delivery of drugs (molecules) to the target.** Targeted drug delivery in cancer therapy will resolve several issues such as protecting drugs from degradation and adverse interactions with biological molecules. Also increasing the selectivity of drug absorption by tumor cells, controlling of pharmacokinetics, increasing bioavailability of drugs into tumor cells. Apart from the drugs nanoparticles can deliver genes into cells.

**2. Treatment and prosthetics using nanomaterials:** The unique properties of nanomaterials allow to produce various implants and dentures. With the use of nanotechnology we can get safe, biocompatible and durable implants.

**3. Diagnostics:** The development of nanotechnology in biomedicine due to improved technology helps to obtain the images, characterization and analysis of biological material, providing a high degree of resolution. Magnetic nanomaterials are an important source for the production of biosensors. The most commonly used nanoparticles are based on the iron oxide coated with various polymers. The surface can be modified by various biospecific ligands as well. Thus the shell protects the iron oxide nanoparticles from chemical interaction with molecules of cells and tissues. Some nanomaterials are also used as electrochemical sensors (nanotubes and nanoparticles) for diagnostics.

**Electronic equipment:**

Nanotechnology in Electronics was given a boost by using carbon nanotubes. They are not only able to replace the transistors, but also give the revolutionary electronic circuits their new mechanical and optical properties to create flexible and transparent electronics. The nanotubes are more mobile and do not hold the light in a thin layer, so that the experimental matrix integrated circuit can be bent without loss of the electronic properties.

Another application of nanotechnology in electronics is the creation of a new type of hard disks. In 2007, the Nobel Prize in Physics was awarded to Peter Grunberg and Albert Fert for the discovery of the giant magneto resistance effect or, as some authors call it, GMR-effect. On the basis of this effect, it is possible to create magnetic field sensors that can exactly read the information recorded on the hard disk with almost the atomic density.

One more prospective application of nanomaterials is producing solar cells. The solar cells that are made on the basis of nanowires instead of the traditional metal wires can increase fifteen times the amount of energy received by a battery. Conductor nanoscale has unique properties of the light absorption. Using nanostructured materials in the manufacturing of the solar cells can improve their efficiency and reduce their cost.

- Silver nanoparticles have good antibacterial properties are used in surgical instruments, refrigerators, air-conditioners, water purifiers etc.

- Gold nanoparticles are used in catalytic synthesis of silicon nanowires, sensors carrying the drugs and in the detection of tumors.
- ZnO nanoparticles are used in electronics, ultraviolet (UV) light emitters, piezoelectric devices and chemical sensors.
- TiO<sub>2</sub> nanoparticles are used as photocatalyst and sunscreen cosmetics (UV blocking pigment).
- Antimony-Tin-Oxide (ATO), Indium-Tin-Oxide (ITO) nanoparticles are used in car windows, liquid crystal displays and in solar cell preparations.
- Nanoscale structures and materials such as nanoparticles, nanowires, nanofibers, and nanotubes have been explored in many biological applications e.g., biosensing, biological separation, molecular imaging, and/or anticancer therapy because of their novel properties and functions differ drastically from their bulk counterparts.
- Their high volume/surface ratio, surface tailorability, improved solubility, and multifunctionality open many new possibilities for biomedicine.
- The intrinsic optical, magnetic and biological properties of nanomaterials offer remarkable opportunities to study and regulate complex biological processes for biomedical applications in an unprecedented manner.
- General applications of these materials are found in water purification, wastewater treatment, environmental remediation, food processing and packaging, industrial and household purposes, medicine and in smart sensor development.
- The nanomaterials are also used in agriculture production and crop protection.
- Nanomaterials prepared from metals, semiconductors, carbon or polymeric species, shaped into nanoparticles and nanotubes have been widely investigated for their ability as electrode modification materials to enhance the efficiencies of electrochemical biosensors.

### 1.10 CARBON NANOTUBES

Carbon is the lightest atom in column IV of the periodic table and is an element with unique and significant properties. It can bind itself or to other light atoms, giving rise to organic chemistry and therefore to biochemistry and the miracle of life on earth. Carbon based materials are unique in several ways. Carbon forms a wide variety of allotropic forms like graphite, diamond, etc.

In 1991, Sumio Iijima presented transmission electron microscopy observations of elongated and concentric layered microtubules made of carbon atoms. This propelled the research related to one of the most actively investigated structures of the last century – nowadays called the carbon nanotubes (CNTs). Following Iijima's ground breaking discovery of multiwall carbon nanotubes (MWCNTs), carbon nanostructures – and in particular carbon nanotubes – have been at the forefront of scientific research in physics, chemistry, materials science, and so on. The discovery of single-wall carbon nanotubes (SWCNTs) in 1993 set yet another milestone in an exponentially growing field. Conceptually, these new nano forms of carbon allotropes with cylindrical geometry belong to the versatile family of fullerenes.

Fullerenes were discovered by Harry Kroto, Robert Curl and Richard Smalley in 1985. This nanometer scale structure was named fullerene due to its resemblance to the highly symmetric

domes designed by the architect Richard Buckminster Fuller. Buckminster fullerenes or fullerenes are the third allotrope of carbon and consist of a family of spheroidal or cylindrical molecules with all the carbon atoms  $sp^2$  hybridized. C<sub>60</sub> was the first fullerene to be discovered. Called the bucky ball, it is a soccer ball (icosahedral) shaped molecule with 60 carbon atoms bonded together in pentagons and hexagons. The carbon atoms are  $sp^2$  hybridized, but unlike graphite, they are not arranged in a plane and is made up of 12 pentagons and 20 hexagons arranged in a spherical shape. The tubular form of the fullerenes are called carbon nanotubes.

Carbon nanotubes have attracted a lot of researchers in a wide range of fields from academia to industry, not only because of their uniqueness when compared with conventional materials, but also because they are very promising materials in nanotechnology.

### 1.10.1 Types of Carbon Nanotubes

A carbon nanotube is a tube-shaped material, made of carbon, having a diameter measuring on the nanometer scale. To understand the structure of a carbon nanotube it can be first imagined as a rolled up sheet of graphene, which is a planar-hexagonal arrangement of carbon atoms distributed in a honeycomb lattice. A single layer of graphite sheet is called graphene.

Carbon Nanotubes have many structures, differing in length, thickness, and in the type of helicity and number of layers. As a group, CNTs typically have diameters ranging from <1 nm up to 50 nm. Their lengths are usually several microns, but recent advancements have made the nanotubes much longer, and measured in centimetres.

There are two types of carbon nanotubes.

1. **Single wall carbon nanotubes (SWCNT):** Single-wall nanotubes (SWNT) are tubes of graphite that are normally capped at the ends. They have a single cylindrical wall. The structure of a SWNT can be visualized as a layer of graphite, a single atom thick, called graphene, which is rolled into a seamless cylinder.

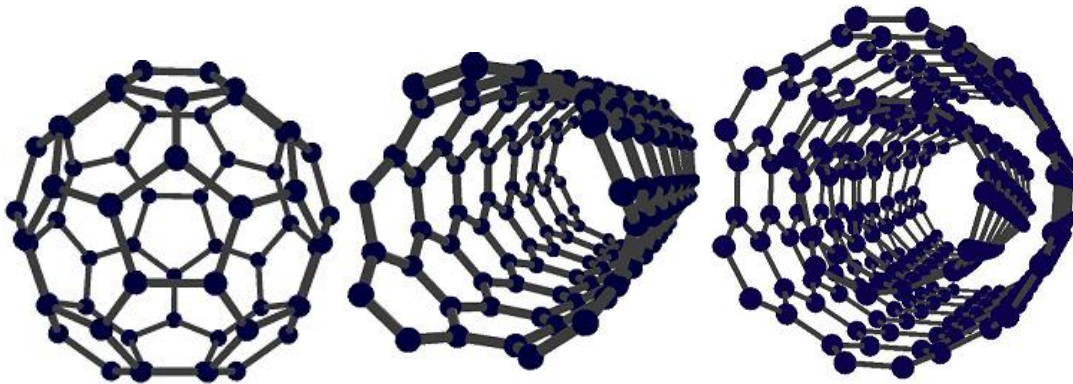
Most SWNT typically have a diameter of close to 1 nm. The tube length, however, can be many thousands of times longer. SWNT are more pliable yet harder to make than MWNT. They can be twisted, flattened, and bent into small circles or around sharp bends without breaking.

2. **Multi wall carbon nanotubes (MWCNT):** There are two structural models of multi wall nanotubes. In the Russian Doll model, a carbon nanotube contains another nanotube inside it (the inner nanotube has a smaller diameter than the outer nanotube). In the Parchment model, a single graphene sheet is rolled around itself multiple times, resembling a rolled up scroll of paper. The simplest representative of a MWNT is a double-walled carbon nanotube (DWNT).

Multi wall carbon nanotubes have similar properties to single wall nanotubes, yet the outer walls on multi wall nanotubes can protect the inner carbon nanotubes from chemical interactions with outside materials. Multi wall nanotubes also have a higher tensile strength than single wall nanotubes.

The diameters of MWNT are typically in the range of 5 nm to 50 nm. The interlayer distance in MWNT is close to the distance between graphene layers in graphite, around 3.39Å.

MWNT are easier to produce than SWNT. However, the structure of MWNT is less well understood because of its greater complexity and variety. Regions of structural imperfection may diminish its desirable material properties.



**Fig. 1.10: Fullerene (C<sub>60</sub>)**

**Single wall CNT**

**Multi wall CNT**

### 1.10.2 Synthesis of carbon nanotubes

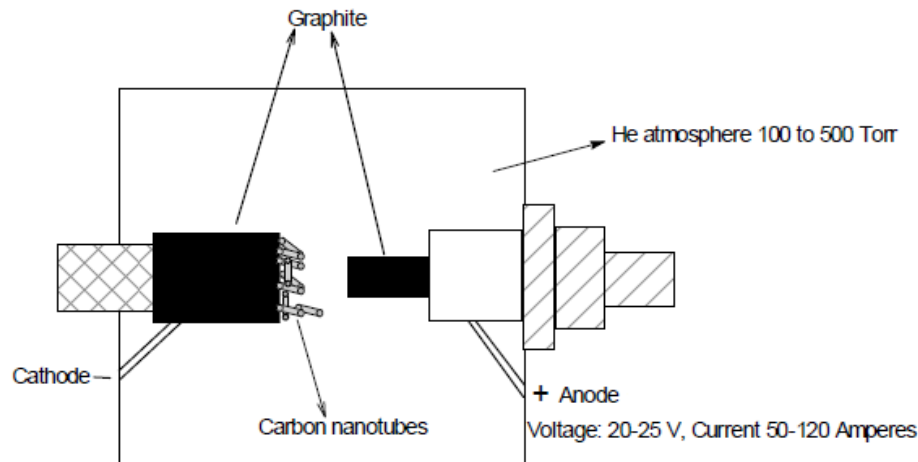
There are several techniques for producing both single wall and multi wall carbon nanotubes and all of them have advantages and disadvantages. Generally, they can be classified into two types depending on whether they require high or medium temperatures.

There are three important methods to produce high quality CNT namely Laser Ablation, Arc Discharge and Chemical Vapour Deposition (CVD). Recently, arc discharge in liquid media has been developed to synthesize several types of nano carbon structures such as carbon onions, carbon nanohorns and carbon nanotubes. This is a low cost technique as it does not require expensive apparatus.

#### 1.10.2.1 Electric Arc Discharge method or Plasma Arcing

The most common method used to fabricate carbon nanotubes is electric-arc discharge. An electric arc is an electrical breakdown of a gas which produces a plasma discharge. The arc occurs in a gas-filled space between two conductive electrodes and it results in a very high temperature, capable of melting or vaporizing almost anything.

A schematic diagram of the arc discharge apparatus for producing CNTs is shown in Fig. 1.11. In this method, two graphite electrodes are installed, and the distance between the two rod tips is usually in the range of 1–2 mm. The anode and cathode are made of pure graphite. The anode is drilled, and the hole is filled with a mixture of metal catalyst powder like iron, cobalt, nickel or yttrium and graphite powder. Then the chamber is filled with a rarefied ambient gas like Helium or Argon using a diffusion pump.



**Fig. 1. 11: Schematic diagram for Electric Arc Discharge method**

The electrical discharge that results brings the temperature up to 6000°C. This temperature is hot enough for the carbon contained in the graphite to sublime. During sublimation, the pressure increases, thus ejecting carbon atoms from the anode and forming a plasma. These atoms move towards the cathode forming a nanotube deposit. If the catalyst metal powders are used, then single wall carbon nanotubes are the dominant product. In the absence of such catalysts, the formation of multi wall carbon nanotubes are favoured.

During the arc-discharge, web-like structures are formed around the cooler parts of the electrodes. Within these structures, bundles of 10-100 single wall carbon nanotubes are formed. This particular method is normally inefficient giving only around 25% pure carbon nanotubes. However, the use of a combined nickel-yttrium catalyst has improved the efficiency and overall production of single wall carbon nanotubes.

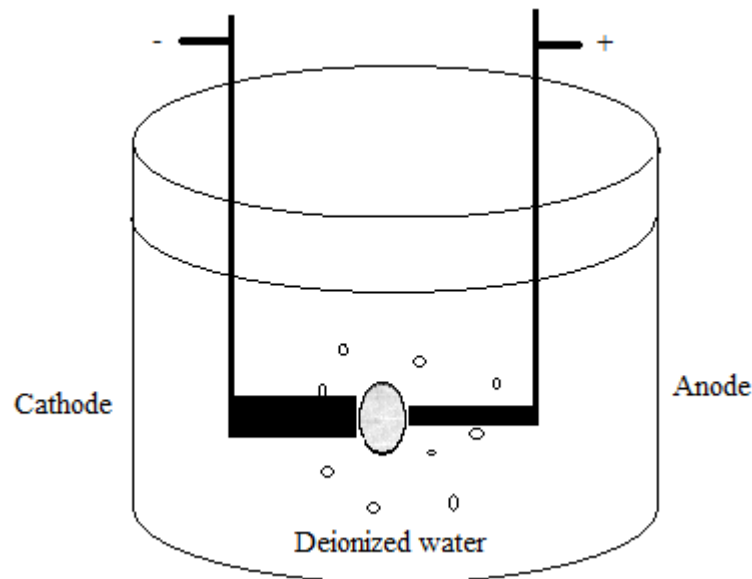
#### 1.10.2.2 Electric Arc Discharge in Liquid Media

The traditional electric arc discharge method used for the production of carbon nanotubes and fullerenes requires complex gas handling equipment, a cooling system, a sealed reaction chamber and several purification processes. However, the growth of arc plasma in water requires simple operation and equipment and has made the process of CNT production more efficient and uniform.

By this method, carbon onions, nanotubes and encapsulates can be produced. A schematic diagram of the arc discharge in liquid media is shown in Fig. 1.12. Two graphite electrodes are installed, and the distance between the two rod tips is usually in the range of 1–2 mm. The diameter of the anode is 6mm and that of the cathode is around 12-20 mm. A 5mm diameter hole was drilled at the open end of the anode and filled with a mixture of graphite and metallic catalyst

powder. Both electrodes are placed in an open vessel which can be filled with liquid nitrogen or deionized water. Initially, the two electrodes touch each other and are connected with a direct current power supply. The arc discharge is initiated by slowly detaching the moveable anode from the cathode. The arc gap is maintained at a distance of 1 mm. Under these conditions, the carbon material sublimating at the anode was deposited as a hard crust at the cathode. The growth rate depends on the applied voltage.

Constant temperature around 25°C is the best thermal condition for synthesizing CNTs by the arc discharge method in liquid. Recently, NaCl solution is also being used as the liquid media to synthesize carbon nanotubes.



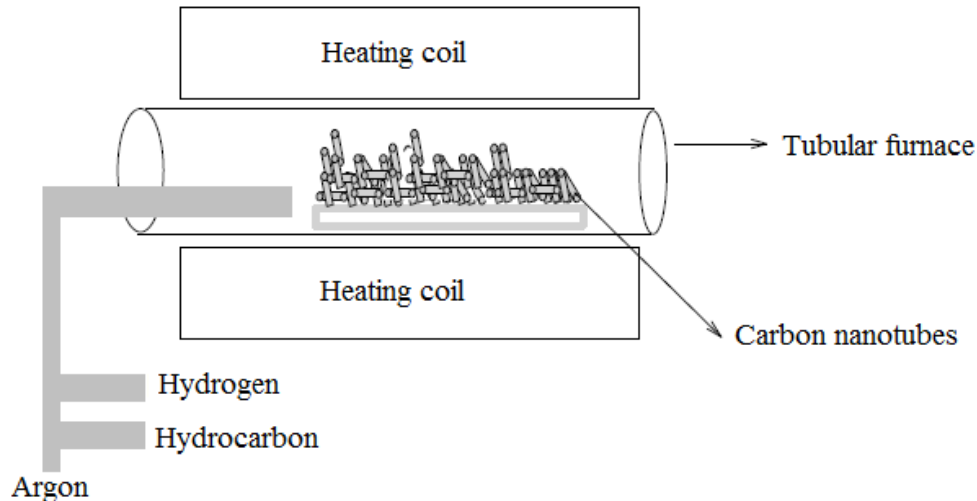
**Fig. 1.12: Electric Arc Discharge method in deionized water**

### 1.10.2.3 Chemical Vapour Deposition (CVD)

Chemical vapour deposition of hydrocarbons over a metal catalyst is a classical method that has been used to produce various carbon materials such as carbon fibres and filaments for over twenty years. It is a versatile method that can produce bulk amounts of defect-free CNTs at relatively low temperatures. In this process, thermal decomposition of a hydrocarbon vapour is achieved in the presence of a metal catalyst. Hence, it is also known as thermal CVD or catalytic CVD.

A schematic diagram of the CVD set up is given in Fig. 1.13. A substrate material like quartz or alumina is taken, cleaned well in preparation for the catalyst deposition and placed in a tubular furnace. A porous substrate is generally used as it enhances the rate of carbon nanotube growth. A catalyst like iron or nickel is deposited on the surface of the substrate through thermal evaporation. The furnace is maintained at a temperature between 600°C and 1200°C. The process involves passing a hydrocarbon vapour (acetylene, ethylene, carbon monoxide, etc.) through the furnace. In the case of a liquid hydrocarbon (benzene, alcohol, etc.), the liquid is heated in a flask and an inert gas is purged through it, which in turn carries the hydrocarbon

vapour into the reaction zone. If a solid hydrocarbon is to be used as the CNT precursor, it can be directly kept in the low-temperature zone of the reaction tube. Volatile materials (camphor, naphthalene, etc.) directly turn from solid to vapour, and perform CVD while passing over the catalyst kept in the high-temperature zone.



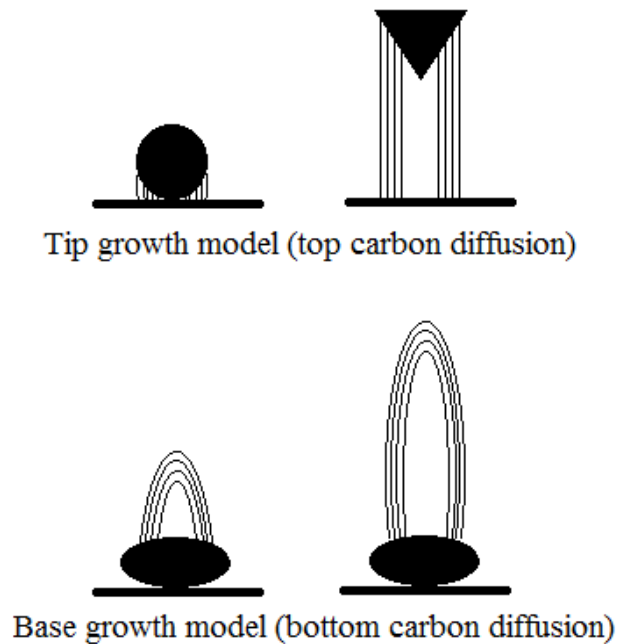
**Fig. 1.13: Chemical Vapour Deposition**

At these high temperatures, carbon dissociates from these precursor molecules and diffuses into the catalyst. CNTs grow on the catalyst in the reactor, which are collected upon cooling the system to room temperature.

There are two basic mechanisms proposed for the growth of nanotubes by the CVD method based on the substrate bound catalyst.

- (i) **Tip growth model (Top carbon diffusion):** The decomposition of the carbon source on the exposed surface of the metal catalyst results in the formation of carbon species. They dissolve in the catalyst and diffuse through it until they precipitate at the end in the form of nanotubes. The catalytic particle sits always on the top of the growing nanotube.
- (ii) **Base growth model (Bottom carbon diffusion):** In this model, the catalyst stays on the substrate. The carbon species dissolve in the catalyst and diffuse through it until they precipitate on top of the metal particle in the form of nanotubes.





**Fig. 1.14: Tip growth and base growth model for growth of carbon nanotubes**

Formation of SWNTs or MWNTs is governed by the size of the catalyst particle. If the particle size is a few nanometers, SWNTs form, whereas if it is larger, MWNTs are formed.

As compared to arc-discharge and laser-ablation methods, CVD is a simple and economic technique for synthesizing CNTs at low temperature and ambient pressure. In crystallinity, arc- and laser-grown CNTs are superior to the CVD-grown ones (although CVD-grown MWCNTs possess inferior crystallinity, the crystallinity of SWCNTs grown by CVD is close to that grown by arc or laser methods). However, in yield and purity, CVD beats the arc and laser methods. And, when it comes to structure control or CNT architecture, CVD is the only answer. CVD is versatile in the sense that it offers harnessing plenty of hydrocarbons in any state (solid, liquid or gas), enables the use of various substrates, and allows CNT growth in a variety of forms, such as powder, thin or thick films, aligned or entangled, straight or coiled nanotubes, or a desired architecture of nanotubes on predefined sites of a patterned substrate. It also offers better control on the growth parameters.

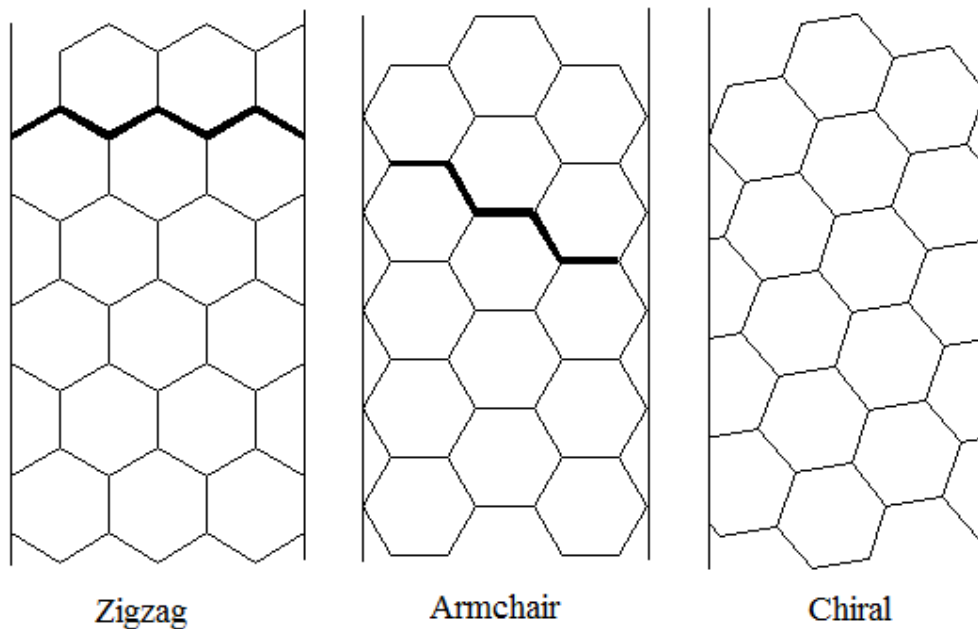
### 1.10.3 Properties of carbon nanotubes

#### 1.10.3.1 Electrical Properties

The electrical properties of carbon nanotubes depend on how the hexagons are orientated along the axis of the tube. Nanotubes can be grouped into different categories based on the amount of twist in the pattern of the carbon atoms around the nanotube's circumference (C). There are three possible orientations – armchair, zig-zag and chiral.

Carbon nanotubes with the hexagons orientated parallel to the axis of the nanotube have electrical properties similar to metals. When a voltage is applied between two ends of an armchair nanotube, there will be a flow of current. An armchair carbon nanotube is, in fact, a better conductor than the copper normally used in electrical wire, or any other metal.

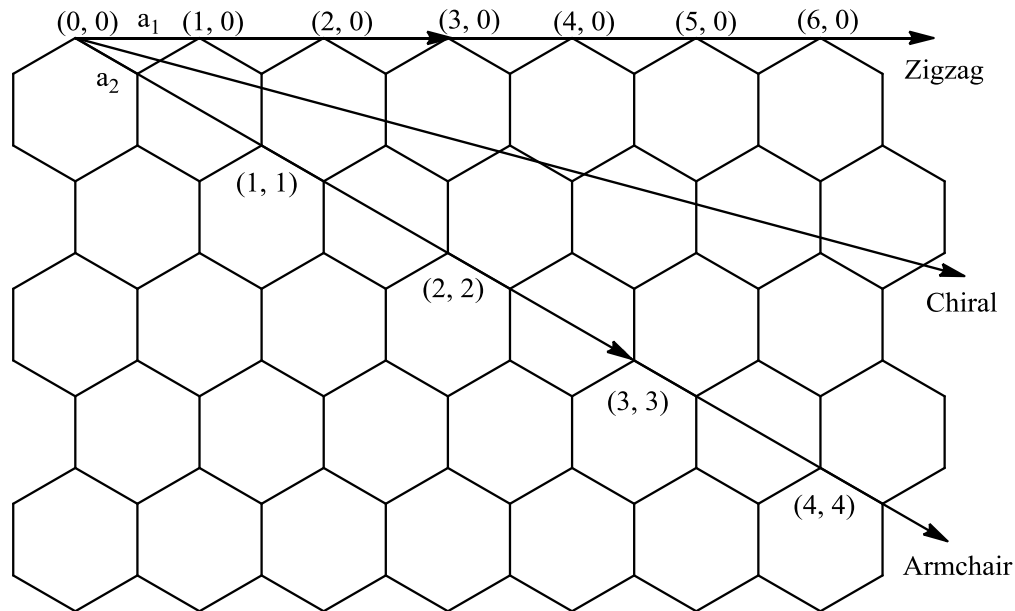
The next two possible orientations of hexagons in carbon nanotubes share electrical properties similar to semiconductors. Those with the hexagons oriented in a circle around the nanotube have a configuration labelled zigzag. Those with a twist to the nanotube so the hexagons do not form any line are called chiral. These two configurations of nanotubes will only conduct electric current when extra energy in the form of light or an electric field is applied to free electrons from the carbon atoms.



**Fig. 1.15: Types of carbon nanotubes**

The electronic properties of a carbon nanotube are determined by its diameter and helicity. A SWCNT is the seamless wrapping of a graphene sheet into a cylinder along the  $(n, m)$  roll-up vector. The  $(n, m)$  indices fully define the SWNT radius and chirality and determine univocally its electronic structure.

Nanotubes form different types, which can be described by the chiral vector  $(n, m)$ , where  $n$  and  $m$  are integers. The chiral vector is given by the diagram in Fig. 1.16. The chiral angle,  $\theta$  is given by  $0 \leq |\theta| \leq 30^\circ$ . Consider a graphene layer where all the carbon atoms in a hexagon is numbered. In a graphene sheet, all carbon atoms with the same numbers are called analogous carbons. The two vectors  $a_1$  and  $a_2$  connect the carbon at the origin to the neighbouring analogous carbon atoms. Since these vectors are not perpendicular to each other, they are named  $a_1$  and  $a_2$ . To name a nanotube, the number of analogous carbons it takes in each direction to get back to the origin carbon atom must be counted. The letter  $n$  is used to indicate the number of analogous carbons in the  $a_1$  direction, and  $m$  is used to indicate the number of analogous carbons in the  $a_2$  direction. The resultant vector is represented by the set of coordinates  $(n, m)$ .



**Fig. 1. 16: Structural representation of metallic and semiconducting carbon nanotubes**

For example: A (3, 0) nanotube ( $n = 3$  and  $m = 0$ ) can be obtained by starting from the origin and moving along three analogous carbons ( $n$ ) in the  $a_1$  direction. If the graphene sheet is rolled up so that the two points (origin and  $n=3$ ) are superimposed on each other, then it is possible to obtain a (3, 0) carbon nanotube.

A (3, 3) nanotube ( $n = 3$ ,  $m = 3$ ) can be obtained by starting at the origin and moving along three analogous carbon in the  $a_1$  direction and then three analogous carbons in the  $a_2$  direction. When these two points (origin and  $n=3$ ,  $m=3$ ) are superimposed on each other, a (3, 3) can be obtained.

The values of  $n$  and  $m$  determine the chirality, or "twist" of the nanotube. The chirality in turn affects the conductance of the nanotube, its density, its lattice structure, and other properties. Hence, based on the type of carbon nanotube, it is possible to determine whether it is metallic or semiconducting. All armchair carbon nanotubes are of the type  $(n, n)$  because of their symmetry and are metallic. The chiral angle of armchair tubes is  $\theta = 30^\circ$ . Zig-zag nanotubes are of the type  $(n, 0)$  with a chiral angle of  $0^\circ$ . They show metallic properties if  $n - m = 3i$ , where  $i$  is an integer, whereas if  $n - m \neq 3i$ , they are semiconducting. For chiral carbon nanotubes, the chiral angle is  $0 < \theta < 30^\circ$ .

Carbon nanotubes are capable of transmitting nearly 1000 times more current than copper.

### 1.10.3.2 Mechanical Properties

Tensile strength is a measure of the amount of force an object can withstand without tearing apart. Carbon nanotubes have been recognized as one of the strongest materials available and their mechanical properties are characterized by Young's modulus and tensile strength.

The tensile strength of carbon nanotubes is approximately 100 times greater than that of steel of the same diameter. There are two things that account for this strength. The first is the strength provided by the interlocking carbon-to-carbon covalent bonds. The second is the fact that each carbon nanotube is one large molecule. This means it doesn't have the weak spots found in other materials, such as the boundaries between the crystalline grains that form steel.

Graphite has an in-plane modulus of 1.06 TPa and due to their carbon-carbon  $sp^2$  bonding, CNTs are expected to show similar stiffness. Single wall CNTs have modulus values in the range of 0.32 to 1.47 TPa and tensile strengths between 10 and 52 GPa whilst multi wall CNTs have modulus values in the range of 0.27 to 0.95 TPa and tensile strengths between 11 and 63 GPa. Its Young's modulus is five times that of steel.

Carbon nanotubes are also lightweight with a very low density of 1.3 to 1.4  $g/cm^3$  depending on the type of CNT. It is one fourth that of steel.

Nanotubes are strong but are also elastic. Researchers have used atomic force microscopes to physically push nanotubes around and observe their elastic properties. Evaluations with transmission electron microscopes show that the bonds in the atomic lattice don't break when a nanotube is bent or compressed.

Carbon nanotubes also conduct heat and cold really well (they have a high thermal conductivity); some researchers predict a thermal conductivity more than 10 times that of silver. While metals depend upon the movement of electrons to conduct heat, carbon nanotubes conduct heat by the vibration of the covalent bonds holding the carbon atoms together; the atoms themselves are wiggling around and transmitting the heat through the material. The stiffness of the carbon bond helps transmit this vibration throughout the nanotube, providing very good thermal conductivity.

### 1.10.3.3 Vibrational Properties

The atoms in a molecule or nanoparticles continuously vibrate back and forth. Each molecule has a specific set of vibrational motions, called normal modes of vibration, which are determined by the symmetry of the molecule.

Carbon nanotubes also have two normal modes of vibration. One mode, labeled  $A_g$ , involves an "in and out" oscillation of the diameter of the tube. Another mode, labeled  $E_{2g}$ , involves a squashing of the tube where it squeezes down in one direction and expands in the perpendicular direction essentially oscillating between a sphere and an ellipse.

The frequencies of the two modes depend on the radius of the tube. These frequencies are now used to measure the radius of the nanotubes.

### 1.10.4 Applications of Carbon Nanotubes

The properties of carbon nanotubes have caused researchers and companies to consider using them in several fields.

- a. Catalyst supports: CNTs can be used as catalyst supports because they can provide higher surface areas and high chemical stability and controlled surface chemistry.

- b. Hydrogen storage: Recently carbon nanotubes have been proposed to store hydrogen in hydrogen-oxygen fuel cell.
- c. AFM Probe tips: To characterize surface of material ‘Probes’ are used. CNTs are widely used a materials for the manufacture of AFM (atomic force microscope) Probes.
- d. Drug Delivery: CNTs can be widely used as drug carriers for drug deliver, as they can easily adapt themselves and enter the nuclei of the cell.
- e. Actuator/Artificial Muscles: An actuator is a device that can induce motion. In the case of a carbon nanotube actuator, electrical energy is converted to mechanical energy causing the nanotubes to move.
- f. Chemical Sensors/Biosensors: Devices used to detect changes in physical and chemical quantities are called sensors. CNTs act as sensing materials in pressure, thermal, gas, optical, mass, position, stress, strain, chemical and biological sensors.
- g. Field Emission: The high current density, low turn-on and operating voltage and steady, long-lived behaviour make CNTs ideal field emitter.
- h. Touch Screens: Very thin CNT films (10 or 20nm) are transparent to visible light and can conduct enough electricity to make them useful for many applications which include thin film solar cells, organic LEDs and touch screens.
- i. Structural and Mechanical Applications: CNTs are characterized with superior mechanical properties such as stiffness, toughness and strength. These properties lead in the production of very strong, lightweight materials that can be sued in areas such as building, structural engineering and aerospace.
- j. Aerospace Components: CNTs have good fatigue strength over a long time which makes use of them as aircraft components.

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### Questions

#### PART - A

- 1) What is VLS mechanism?
- 2) What are nanowires?
- 3) What are the two steps of VLS mechanism?
- 4) Draw the schematic diagram of synthesis of nanowires.

- 5) List any two conditions of the catalyst used in the VLS mechanism.
- 6) Write any two applications of nanowires.
- 7) What are nanoporous materials? Give examples.
- 8) Write the classification of nanoporous materials.
- 9) Write the basic principle of sol-gel process.
- 10) List any two advantages of sol-gel process.
- 11) What are the applications of sol-gel process?
- 12) What are the precursors used in the sol—gel process? Give examples.
- 13) Write the various steps involved in the sol-gel process.
- 14) List any two properties of nanoporous materials.
- 15) Specify any two applications of nanoporous materials.
- 16) What are advantages of CVD process?
- 17) What is the basic principle of CVD process?
- 18) What are the precursors used in CVD process?
- 19) Specify any two types of CVD process.
- 20) Mention the applications of CVD method.
- 21) What is PVD? Mention the various methods of PVD.
- 22) List any two advantages of PVD process.
- 23) Write any two applications of PVD process.
- 24) What is the role of nanomaterials in the field of nuclear power engineering?
- 25) Write a short note on the role of nanomaterials in material surface protection.
- 26) What are carbon nanotubes ?
- 27) Differences between SWCNT and MWCNT.
- 28) How are CNTs classified based on chirality or helicity or asymmetry?
- 29) Mention the application of CNTs.
- 30) Define top-down nanofabrication and bottom-up nanofabrication.
- 31) What are the unique properties of CNTs?

#### **PART - B**

- 1) Describe the synthesis and application of nanowires.
- 2) What are nanoporous materials? How are nanoporous materials synthesized by sol-gel method?
- 3) Explain briefly the advantages and applications of sol-gel process.
- 4) Discuss the main properties and applications of nanoporous materials.
- 5) Describe briefly the synthesis of nanomaterials by chemical vapour deposition process.
- 6) List the advantages and applications of chemical vapour deposition process.
- 7) What is CVD? Explain the different types of CVD reactors, mechanism of CVD.
- 8) What is PVD? Explain the basic principles of any two PVD methods.
- 9) Describe the advantages and applications of chemical vapour deposition process.
- 10) Discuss broadly about the applications of nanomaterials.
- 11) Write an account of carbon nanotubes.
- 12) Explain the electrical properties of carbon nanotubes.
- 13) Write the mechanical properties of CNTs.

14) Explain the synthesis of CNTs.