

## CHAPTER - 7

# NANOMATERIALS

*Nanomaterials: Synthesis - Plasma arcing - Pulsed laser deposition - Chemical vapour deposition - Sol-gel - Electrodeposition - Ball milling - Properties of nanoparticles and applications.*

*Carbon nanotubes: Structure - fabrication - Arc method - Pulsed laser deposition - Chemical Vapour deposition - Properties and applications.*

## 7.1 NANOTECHNOLOGY

### 7.1.1. Nanomaterials ✓

*Nanoparticles are the particles that have three dimensional nanoscale, i.e., the particle is between 1 and 100 nm in each spatial dimension. A nanometer is a unit of measure equal to one-billionth of a meter, or three to five atoms across.*

*Nanotechnology is the design, fabrication and use of nanostructured systems, and the growing, assembling of such systems either mechanically, chemically or biologically to form nanoscale architectures, systems and devices. Small features permit more functionality in a given space, so nanotechnology is a continuation of miniaturization from micron meter scale down to nanometer scale. Materials in this size exhibit some different physical properties. For example, crystal in the nanometer scale have a low melting point and reduced lattice constant.*

*Nanostructured materials can be made with unique nanostructures and properties. This field is expected to open new venues in science and technology.*

### 7.1.2. Comparison of Different Objects

1. Diameter of sun	- 1,393,000 km
2. Diameter of earth	- 12,800 km
3. Height of Himalaya mountain	- 8,848 m
4. Height of man	- 1.65 m
5. Virus	- 20 - 250 nm
6. Cadmium sulphide nanoparticle	- 1 - 10 nm



### 7.1.3. Classification of Nanomaterials ✓

As the field of nanostructured materials has evolved, many names and labels have been used.

#### 1. Clusters

A collection of atoms or reactive molecules up to about 50 units.

#### 2. Colloid

A stable liquid phase containing particles in 1 to 1000 nm range. A colloidal particle is one such 1 to 1000 nm sized particle.

#### 3. Nanoparticle

A solid particle in the 1 to 100 nm range that could be non-crystalline, an aggregate of crystallites, or a single crystallite.

#### 4. Nanocrystal

A solid particle that is a single crystal in the nanometer size.

#### 5. Nanostructured or Nanoscale Material

Any solid materials has a nanometer dimension.

Three dimensions → Particles ✓

Two dimensions → Thin films ✓

One dimension → Thin wire. ✓

#### 6. Quantum Dots

A particle that exhibits a size quantization effect in at least one dimension.

### 7.1.4. Top-down and Bottom-up Processes

There are two processes for the synthesis of the nanophase materials:

1. Top-down processes
2. Bottom-up processes.

#### 1. Top-down Processes

In this processes, bulk materials are broken into nano sized particles as shown in Fig. 7.1.

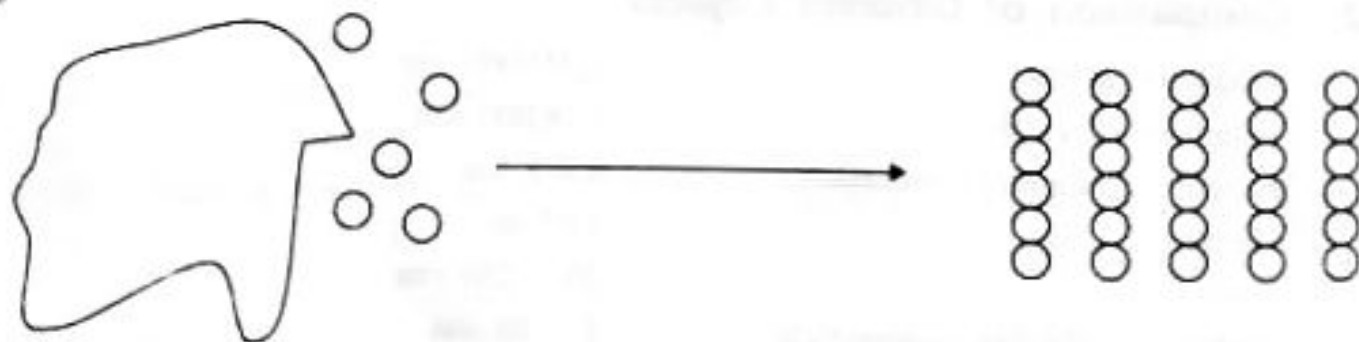


Fig. 7.1. Assembly from Bulk Materials



*In top-down processes, the building of nanostructures starting with small components like atoms and molecules that are removed from a bulk material so as to obtain desired microstructure.*

**Examples** Nanolithography, Ball milling, etc.

**(i) Advantages**

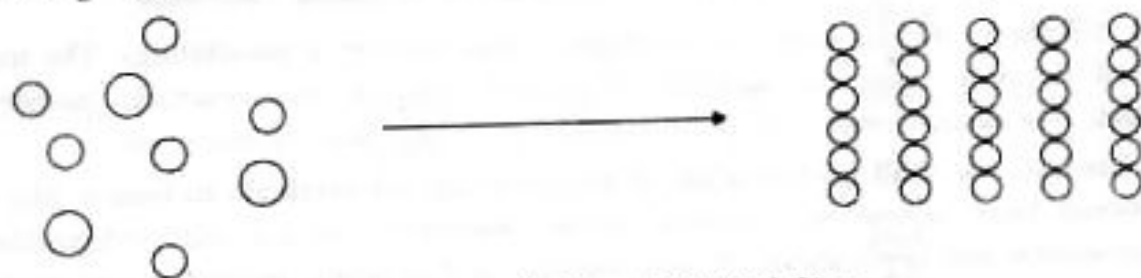
1. The main advantage is that the covalent bonds holding together a single molecule which is far stronger.
2. This is mostly used by chemist to create structure by connecting molecules.

**(ii) Limitations**

1. Cost of new machines and clean room environments grows exponentially with newer technologies.
2. Physical limits of photolithography is another problem.
3. With smaller geometries and conventional materials, heat dissipation is also a problem.

**2. Bottom-up Processes**

In this processes, nano phase materials are produced by building of atom by atom as shown in Fig. 7.2.



**Fig. 7.2. Assembly from Individual Atom**

*This processes building larger objects from smaller building blocks. Nanotechnology seeks to use atoms and molecules as those building blocks. This is the opposite of the top-down approach. Instead of taking material away to make structures, the bottom-up approach selectively adds atoms to create structures.*

**Examples** Pulsed laser deposition, Chemical vapour deposition, etc.

**(i) Advantages**

1. Allows smaller geometries than photolithography.
2. Certain structures such as carbon nanotubes and Silicon nanowires are grown through a bottom-up process.
3. New technologies such as organic semiconductors employ bottom-up processes to pattern them.
4. It can make formation of films and structures much easier.
5. This is more economical than top-down. It does not waste the material to etching.



## 7.2 SYNTHESIS TECHNIQUE ✓

There are a large number of technique available to synthesize different types of nanomaterials in the form of colloids, clusters, powders, tubes, rods, wires, thin films etc.

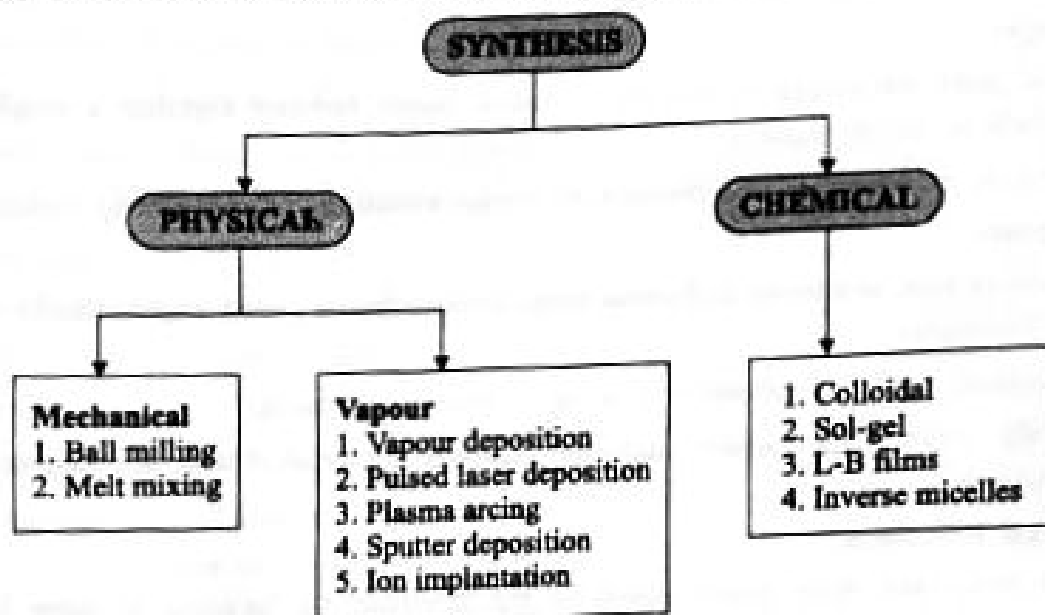


Fig. 7.3. Different Types of Nanomaterials Synthesis Technique

Fig. 7.3 shows that for each type there are a large number of possibilities. The technique to be used depends upon the material of interest, type of nanostructures namely, zero dimensional, one dimensional or two dimensional materials, size, quantity etc.

In this unit, we shall discuss some of the nanomaterials synthesis technique like plasma arcing, pulsed laser deposition, chemical vapour deposition, sol-gel, electrodeposition, ball milling, properties and applications of nanomaterials, and structure, properties and applications of the Carbon nanotubes.

### 7.2.1. Plasma Arcing

This is one of the simplest and useful methods, which leads to mass-scale production of Fullerenes and Carbon tubes.

#### 1. Plasma

*Plasma is an ionized gas. It is a mixture of free electrons, ions and photons. It is overall neutral but there can be regions, which are predominantly of positive or negative charges. Plasma is achieved by making a gas conduct electricity by providing a potential difference across the two electrodes so that the gas yields up its electrons and thus ionizes.*

#### 2. Principle

*Plasma is created by vaporizing an electrode in the two electrode system using a low voltage difference at a high current. Positive electrode (anode) acts as the source of materials. The atoms in anode are ionized. The ions leave the anode and are deposited on the cathode. The ions are usually passed through an inert gas.*



2. The plume of ablated material is highly forward directed, which causes poor conformal step coverage. It also makes thickness monitoring difficult.
3. Target surface modification is difficult.

## 5. Applications

1. It is used to prepare the ceramic films like YBCO, PZT etc.
2. It is used to produce the hard coating like diamond-like films (TiC, SiC, SiO<sub>2</sub> etc.).
3. Exotic alloys and multi-component films like Fe<sub>16</sub>N<sub>2</sub>, La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> are prepared by this technique.
4. Multilayer films like superlattice, hetero-structures, graded layers etc. are prepared by this technique.

### 7.2.3. Chemical Vapour Deposition (CVD) ✓

Chemical Vapour Deposition (CVD) involves the reaction or decomposition of vapour phase species at elevated temperatures and subsequent deposition from a vapour by a chemical reaction occurring on a heated substrate surface.

#### 1. Principle

*Precursor gases are delivered into the reaction chamber at elevated temperature usually under vacuum. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase. They are deposited onto the substrate. The substrate temperature is critical and can influence what reactions will take place.*

#### 2. Different Types

1. Atmospheric Pressure Chemical Vapour Deposition (APCVD)
2. Low Pressure Chemical Vapour Deposition (LPCVD)
3. Metal Organic Chemical Vapour Deposition (MOCVD) ✓
4. Plasma Assisted Chemical Vapour Deposition (PACVD) or Plasma Enhanced Chemical Vapour Deposition (PECVD)
5. Laser Chemical Vapour Deposition (LCVD)
6. Photochemical Vapour Deposition (PCVD)



### 3. Construction and Working

Chemical vapour deposition processes are distinguished from PVD by the fact that growth proceeds as a result of a series of chemical reactions above the heated substrate. Further, CVD process can be considered as near equilibrium growth phenomenon while PVD is clearly very far from an equilibrium process.

Fig. 7.6 shows the apparatus used in the CVD process for a thin film single crystal growth on the Silicon wafer. The basic chemical reaction used to describe the epitaxial growth of pure Silicon is the hydrogen reduction of Silicon tetrachloride.

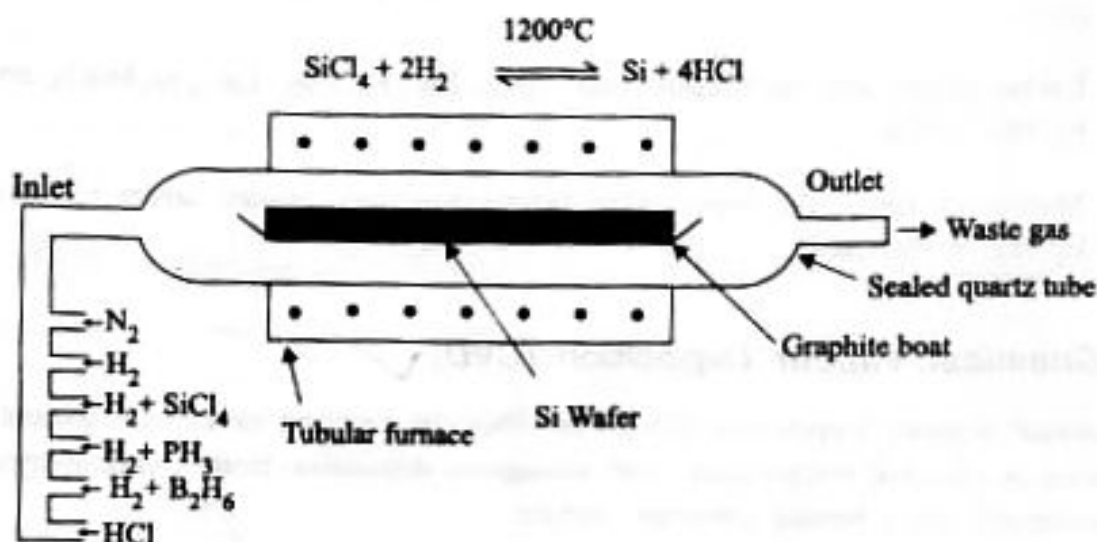


Fig. 7.6. Chemical Vapour Deposition

A CVD apparatus will consist of several basic components:

1. **Gas delivery system** : For the supply of precursors to the reactor chamber.
2. **Reactor chamber** : Chamber within which deposition takes place.
3. **Substrate loading mechanism** : A system for introducing and removing substrates, etc.
4. **Energy source** : Provide the energy/heat that is required to get the precursors to react/decompose.
5. **Vacuum system** : A system for removal of all other gaseous species other than those required for the reaction/deposition.
6. **Exhaust system** : System for removal of volatile by-products from the reaction chamber.



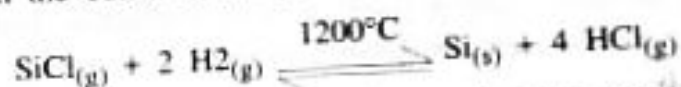
The following steps are involved in the chemical vapor deposition:

1. Vaporization and transport of precursor molecules into reactor.
2. Diffusion of precursor molecules to the surface of particle.
3. Adsorption of precursor molecules to the surface of particle.
4. Decomposition of precursor molecules on the surface and incorporation into solid films.

**Example-1: Deposition of Silicon** (Write any one example for examination)

A Quartz tube is sealed inside the tabular R.F. induction coil furnace. There is a Graphite boat carries the Silicon crystal wafer on which epitaxy layer should be grown. At the inlet of the Quartz tube along with the Hydrogen and Silicon tetra chloride gases, some impurity gases like Phosphine ( $\text{PH}_3$ ) for n-type doping and Biborane ( $\text{B}_2\text{H}_6$ ) for p-type doping also introduced at approximately  $1200^\circ\text{C}$ .

There is a control console which permits only the required gases at suitable pressures so that it is possible to form an almost abrupt step p-n junction by this process. The waste gases are escaped from the outlet of the Quartz tube.

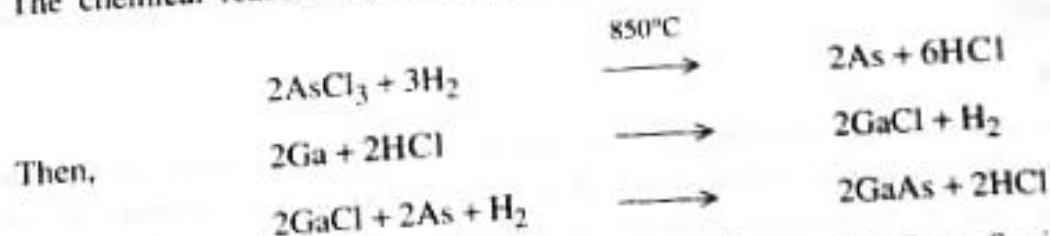


This reaction is reversible, and the growth rate depends strongly upon the proportion of the two source gases. Growth rates about 2 micrometers per minute produce polycrystalline Silicon.

**Example-2: Deposition of GaAs**

For GaAs growth, the source materials are elemental Ga and  $\text{AsCl}_3$ . Hydrogen gas acts as a carrier gas. The  $\text{AsCl}_3$  is put in bubbles through which Hydrogen is passed. The resulting gas flows over the Ga source and then onto the substrate.

The chemical reaction is as follows:



In the GaAs growth, Zinc is used for p-type doping and S or Se is used as n-type dopant. Usually gas pressures in the range from 0.1 to 1.0 torr are used. Growth range and film quality depend upon the gas pressure and the substrate temperature. When the growth takes place at low temperature, it is limited by kinetics of surface reaction. At intermediate temperature, it is limited by mass transport i.e., supply of reacting gases to the substrate.



Here the reaction is faster and supply of reactants is slower. At high temperature, growth rate reduces due to desorption of precursors from the substrate.

#### 4. Advantages

1. CVD coatings are typically fine grained, high purity, and harder than similar materials produced using conventional ceramic fabrication processes.
2. CVD coatings are usually only a few microns thick. The rate of deposition is of the order of a few hundred microns per hour.
3. CVD is an extremely versatile process that can be used to produce almost any metallic or ceramic compounds.

#### 5. Applications

Some of the applications of CVD are as follows:

1. It is used to produce the nanomaterials like Metals and Alloys, Carbides, Nitrides, Borides, Oxides, and Intermetallic compounds.
2. CVD has variety of applications across a wide range of industries.
3. It is used to produce coatings such as wear resistance, corrosion resistance, high temperature protection, erosion protection etc.
4. It can be used to produce the semiconductors and related devices like integrated circuits, sensors and optoelectronic devices.
5. It is used in optical fibers which are used for telecommunications.
6. It is used in the production of novel powders and fibers, catalysts, nano-machines.

### 7.2.4. Sol-gel Method ✓

As the name suggests sol-gel involves two types of materials 'sol' and 'gel'. Sol-gels are known since the time when M.Ebelman synthesized them in 1845. It has considerable interest both in scientific and industrial field because of the several advantages as compared to other techniques.

#### 1. Sol and Gel

Sol-gel is a useful self assembly process for nanomaterials formation. *Solid particles that is suspended in a liquid is called a sol (Fig. 7.7a). Thus it is a subclass of colloids. Gels are nothing but a continuous network of particles with pores filled with liquid or polymer containing liquid (Fig. 7.7b). A sol-gel process involves formation of sols in a liquid and then connecting the sol particles to form a network (Fig. 7.7c).* By drying the liquid, it is possible to obtain powder, thin films or even monolithic solid. Sol-gel method is particularly useful to synthesis Ceramics or Metal oxides although Sulfides, Borides and Nitrides.



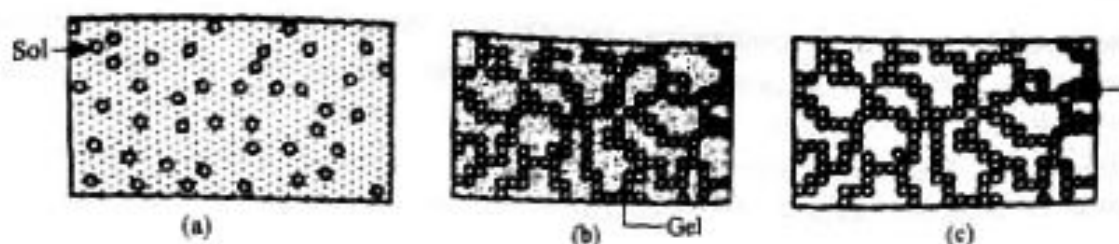


Fig. 7.7. (a) Sol, (b) Gel, and (c) Monoclinic Solid (Aerogel)

## 2. Synthesis of Sol-gel

Synthesis of sol-gel involves hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process by various routes as shown in Fig. 7.8.

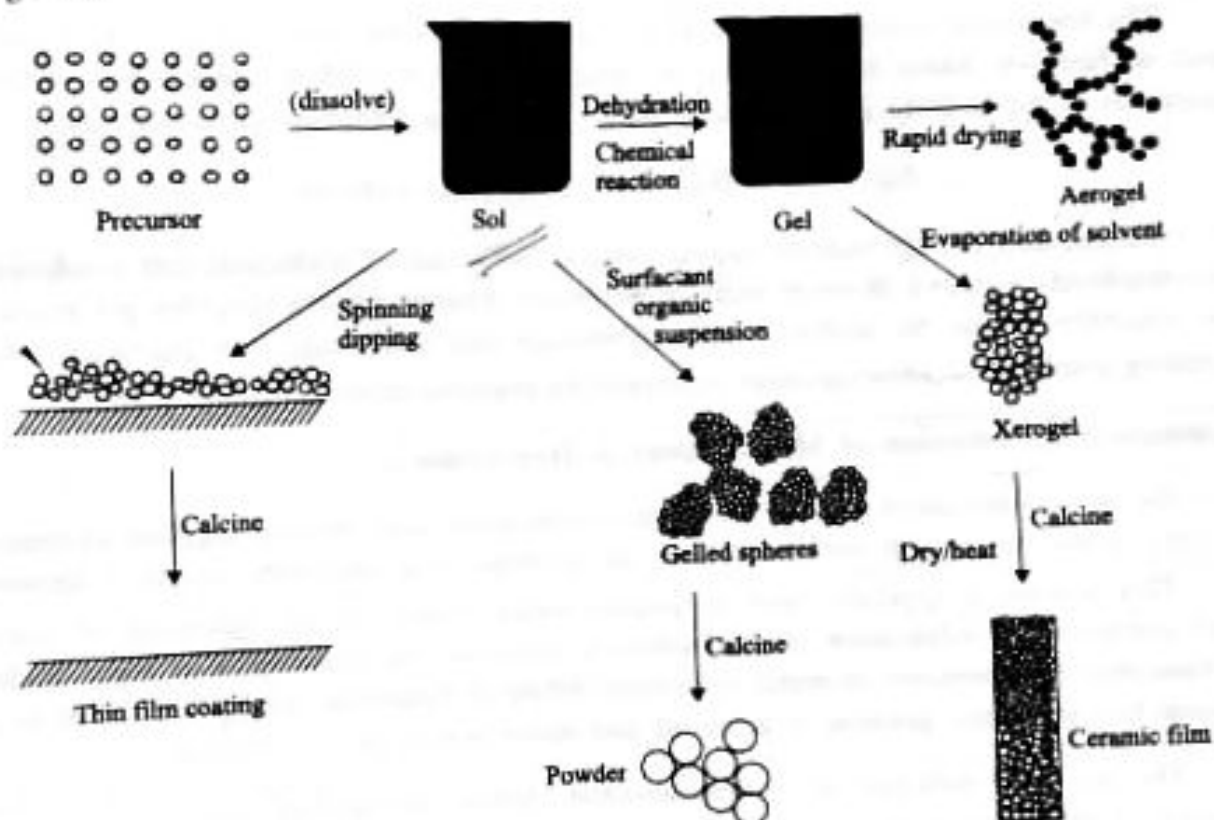


Fig. 7.8. Summary of Sol-gel Process

Starting materials are the precursors. They are to be chosen so that they have a tendency to form gels. Both alkoxides and metal salts can be used as precursors. Mixtures of precursors can also be used to produce binary or ternary systems. Each molecular precursor having its own reaction rate that is dependent on pH, concentration, solvent and temperature.

Further processing usually involves forming the gel using a number of techniques followed by gentle drying to remove the solvent (this often leads to shrinkage). Gels can be



cast and moulded to form a microporous preform and dried to produce a monolithic bulk material e.g., a xerogel or an aerogel. They can also be spin coated or dipped to produce thin (typically 50–500 nm) films on substrates. The interconnected nanoscale porosity in the dried gel can be filled via incorporation of a second material using techniques such as liquid infiltration or chemical reaction. These materials may then be classed as nanocomposites.

Hydrolysis and drying are two key steps in determining the properties of the final product in sol-gel processing. The rate of the hydrolysis and condensation are important parameters that affect the properties of the final product. Slower and more controlled hydrolysis typically leads to smaller particle sizes and more unique properties.

#### **Example-1: Production of $\text{SiO}_2$**

(Write any one example for examination)

The best known example of a sol-gel process is probably the production of  $\text{SiO}_2$ . A catalyst (acid or basis) is added to a solution of tetramethoxysilane (TMOS), water, and methanol. Hydrolysis of the Si-OMe (Me – Methyl) bonds leads to the formation of Si-OH groups:



Further dehydration reduces the  $\text{Si}(\text{OH})_4$  to  $\text{SiO}_2$  gel. If hydrolysis and condensation are completed, a silicon di-oxide xerogel is formed. During the reaction, the gel reaches a low viscosity. It can be applied onto a centrifuge and distributed over the water. When annealing over  $800^\circ\text{C}$ , homogeneous oxides can be manufactured.

#### **Example-2: Production of Metal Oxides & Hydroxides**

By polycondensation process (i.e., many hydrolyzed units coming together by removal of some atoms from small molecules) sols are nucleated and ultimately sol-gel is formed.

This process is typically used to prepare metal oxides via the hydrolysis of reactive metal precursors. Condensation of the hydroxide molecules by elimination of water leads to the formation of a network of metal hydroxide. When all hydroxide species are linked in one network like structure, gelation is achieved and dense porous gel is obtained.

The gel is a polymer of a 3-dimensional skelton surrounding interconnected pores. Removal of the solvents and approximate drying of the gel results in an ultrafine powder of the metal hydroxide. Further heat treatment of the hydroxide leads to the corresponding powder of the metal oxides. Since the process starts with a nanosized unit, and undergoes reactions on the nanometer scale, the final product is also in the nanoscale.

### **3. Advantages**

The following are the advantages of the sol-gel process:

1. It is economical route.
2. It generates highly pure, well controlled ceramics compared to other techniques.



3. It is a low temperature process i.e., it has less energy consumption and low pollution.
4. The instrument processing is easy and synthesis almost all the materials.
5. It is possible to get the unique materials like Zerogels, Zeolites, Ordered porous solids by organic / inorganic hybridization.
6. It is also possible to synthesis nanoparticle, nanorods, nanotubes etc. using this technique.

#### 4. Disadvantages

1. It has weak bonding and low wear resistance.
2. Here, it is difficult to control the porosity.
3. It has high permeability.

#### 5. Applications

The following are some of the applications of this sol-gel process:

1. The nanomaterials produced by this technique are used for electronic thin film devices, for wear, chemical or oxidation protection, as well as for their optical properties (e.g., anti-reflection).
2. This method is used to produce the lightest materials.
3. Optical coating, protective and decorative coatings can be done by this method.
4. Sol-gel routed ceramic fibers are used for fiber optic sensors and thermal insulation.
5. The ultra fine particle prepared by this technique is used for dental and biomedical applications.
6. Silicate sol is formed by this method.

### 7.2.5. Electrodeposition ✓

#### 1. Definition

Electrodeposition is in the process that exploits the creation of solid materials directly from electrochemical reactions in liquid compositions with substrate materials. This is one of the chemical methods. Electrodeposition is also known as electroplating.

#### 2. Principle

*Substrate is placed in electrolyte. When an electrical potential is applied between a conducting area on the substrate and a counter electrode in the liquid, a chemical redox process takes place resulting in the formation of a layer of material on the substrate and usually some gas generation at the counter electrode.*



### 3. Experimental Set-up and Working

The experimental arrangement of the electrodeposition consists of a three-electrode electrochemical cell (a reference electrode, a cathode, and a counter electrode), porous membrane, electrolyte and a.c. or d.c. power supply as shown in Fig. 7.9. The electrolyte is an aqueous solution. The power supply is used to apply controlled current at a certain voltage.

When the current is allowed to pass through the three electrode electrochemical cell, a certain amount of atoms are liberated from anode and is deposited on the surface of the cathode. The surface morphology of the deposits depends on the surface structure and chemical composition of the cathode substrate as well as other electrochemical parameters.

The final size distribution of the electrodeposits strongly depends on the kinetics of the nucleation and growth:

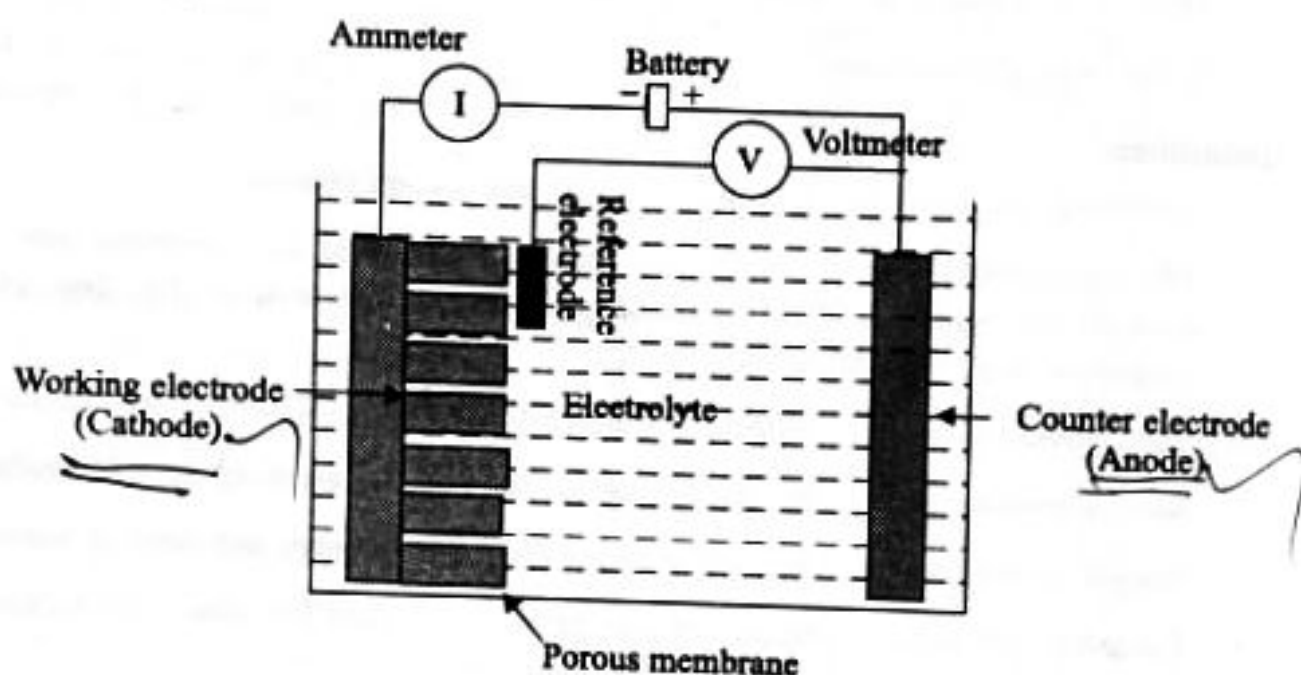


Fig. 7.9. Experimental Arrangement - Electrodeposition

#### (i) Instantaneous Nucleation

All the nuclei form instantaneously on the electrode substrate, and subsequently grow with the time of electrodeposition.

#### (ii) Progressive Nucleation

The number of nuclei that are formed is a function of time of electrodeposition. These nuclei gradually grow and overlap, and therefore, the progressive nucleation process exhibits zones of reduced nucleation rate around the growing stable nuclei.



**(iii) Growth**

The formation of nanostructures results from growth of the nuclei that invariably nucleate at the holes and defects of the electrode substrate. Subsequent growth of these nuclei yields the desired surface morphology of the nanostructures, which can therefore be synthesized by choosing the appropriate surface of the electrode.

**Examples** Nano-porous polymers, Porous Alumina etc.

**4. Advantages**

1. Electrodeposition is relatively cheap.
2. It can be performed at low temperatures which will minimize inter-diffusion in the preparation of multilayered thin film.
3. The film thickness can be controlled by monitoring the amount of charge delivered, and the deposition rate can be controlled by the variation of the current with time.
4. The composition and defect chemistry can be controlled by the magnitude of the applied potential.
5. The applied current in a solution containing a mixture of precursors allows the production of a multilayered material.
6. It is an important technique for synthesizing metallic nanomaterials with controlled shape and size.
7. It is used to prepare nanometer-sized particles, fibers, wires, rods, and tubes.

**5. Disadvantages**

1. It requires electrically conducting substrate materials.
2. If the growth is epitaxial, then any strain due to lattice mismatch between the nanocrystal, and the substrate can be growth-limiting.
3. It is difficult to prepare the desired templates
4. High temperature annealing steps are expensive and unsuitable for polymer substrates.

**6. Applications**

1. This technique is used to produce the nano-indented holes, meso-porous silica, nanoporous polymers, porous alumina.
2. This is a versatile technique to synthesize various kinds of nanomaterials with desired surface morphologies (nanorods, nanoparticles, and nanowires).



### 7.2.6. Ball Milling ✓

Ball mill is an efficient tool to grind many kinds of mine and other materials into fine powder. It is one of the simplest method and widely used in building materials, chemical field, industry etc.

#### 1. Principle

*Ball milling is a process that produce a wide range of new light materials by simply mixing two elemental powders and mechanically milling them as shown in Fig. 7.10, in a high energy environment such as a ball mill. The action of the ball mill generates sufficient controllable heat to make supersaturated and stable alloys that are economic to produce in large quantity.*

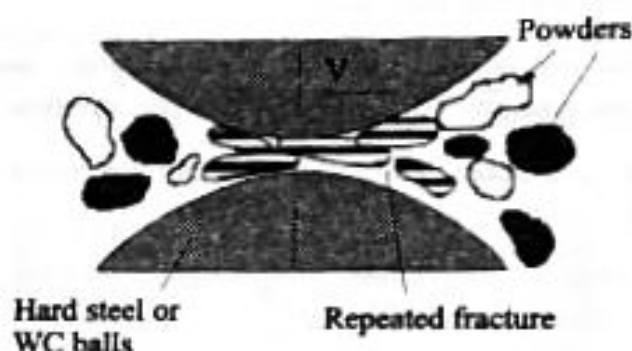


Fig. 7.10. Principle of Ball Mill

#### 2. Construction

There are many types of ball mills are available namely, planetary, vibratory, rod etc. Usually one or more containers are used at a time to make fine particles.

Size of the container depends upon the quantity of interest. Hard Steel or Tungsten Carbide (WC) balls are put into container as shown in Fig. 7.11 along with powder of material. Initial material may be arbitrary size and shape. Container is closed with tight lids. Usually 2:1 mass ratio is advisable.

If the container is more than half filled, the efficiency of milling is reduced. The container may be filled with the gases like  $O_2$ ,  $N_2$  or inert gas. It can be add some additional impurity into the powder, if proper precaution is not taken. A temperature rise in the range of 100 to 1100°C is expected to take place during the collisions. Lower temperatures favour amorphous particle formation. Low temperature cooling is used sometimes to dissipate the generated heat.



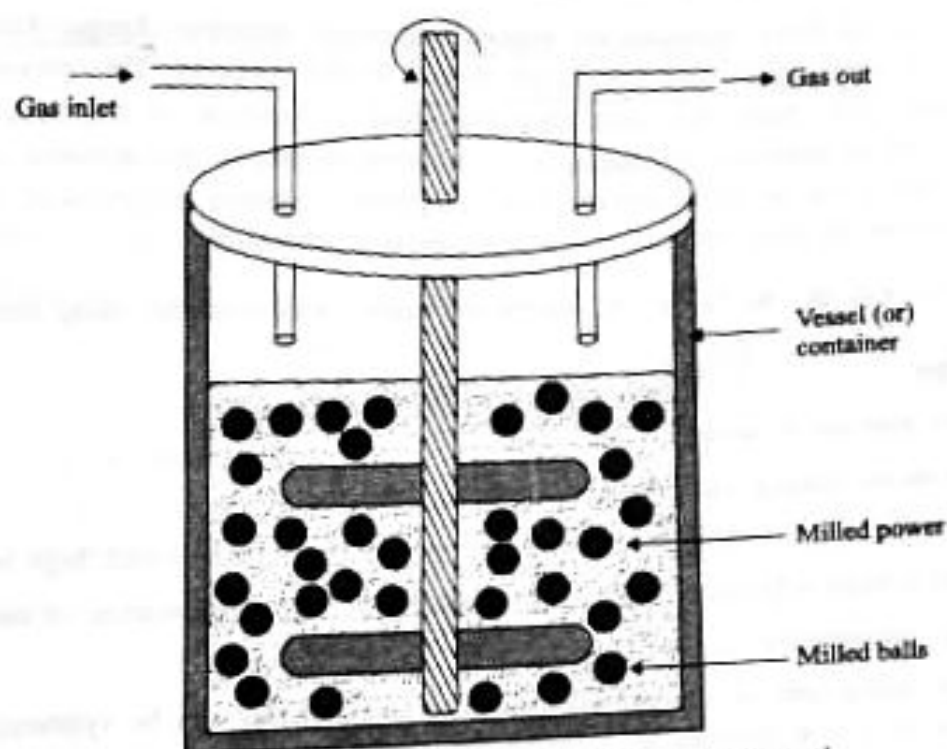


Fig. 7.11. A Schematic Diagram of Ball Mill Vessel

### 3. Working

The containers are rotated at high speed from 300 to 600 rpm around their own axis. Additionally, they may rotate around the central axis. When the containers are rotating around the central axis, the material is forced to the walls and is pressed against the walls. But due to the motion of the containers around their own axis, the material is forced to other region of the container, as illustrated in Fig. 7.12. Fig. 7.12 shows the material thrown against the wall during the rotation of a single container. Dark regions are illustrating the powder material, while the rest is empty.

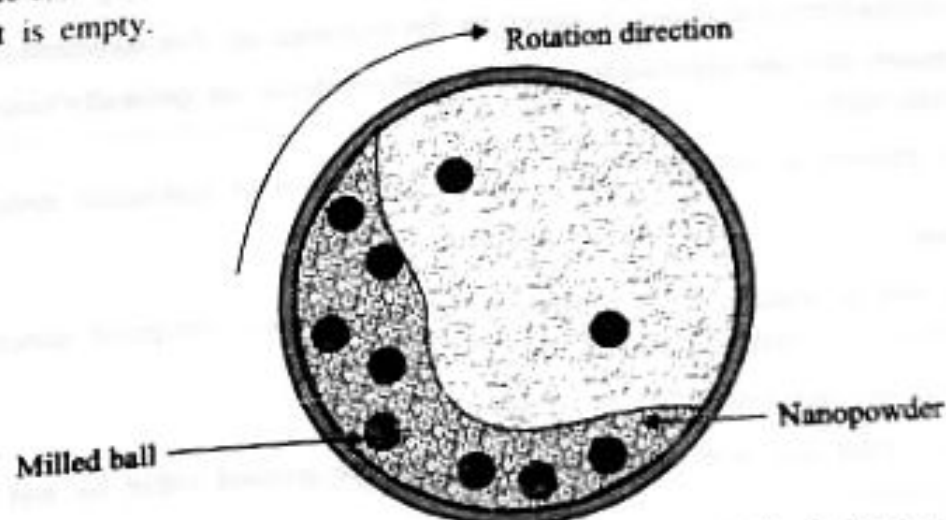


Fig. 7.12. Schematic Diagram of Rotation of Ball in the Container



✱ Heavy milling balls increase the impact energy on collision. Larger balls used for milling, produce small grain size and larger defects in the particles. This process may add some impurities from balls. By controlling the speed of rotation of the central axis and container as well as duration of milling, it is possible to ground the material to fine nano sized powder and it can be quite uniform. Few milligrams to several kilograms of nanoparticles can be synthesized in short time of a few minutes to a few hours.

**Examples** Co, Cr, W, Ni-Ti, Al-Fe, Ag-Fe are made nanocrystalline using this technique.

#### 4. Advantages

1. This process is simple.
2. It can be readily implemented commercially.
3. This technique produces ultra-fine nanocrystalline materials with high homogeneity.
4. It is a high efficient technique to synthesis a large combination of materials.
5. It is inexpensive.
6. Few milligrams to several kilograms of nanoparticles can be synthesized in short time of a few minutes to a few hours.
7. It is applicable to synthesis all classes of materials including metal oxides.

#### 5. Disadvantages

1. The container may be filled with the gases like  $O_2$ ,  $N_2$  or inert gas. It can be add some additional impurity into the powder, if proper precaution is not taken.
2. The grinding balls contribute to impurities.
3. Larger defects in the particles may occur when heavy milling balls are used.
4. Microstructures and phases produced by this technique are thermodynamically metastable.
5. Materials that are affected by metallic contamination are generally cannot be handled in ball mill.
6. This process is very restrictive for the production of non-oxide materials.

#### 6. Applications

1. Ball mill is widely used to produce Silicate product, fire-proof materials, chemical fertilizer, non-ferrous metals, glass, Ceramics etc.
2. It is a key equipment for re-grinding.
3. It can grind any type of materials that can be grinded either by wet process or by dry process.
4. Intermetallic compounds based on Nickel and Aluminum can be produced.



## 7.3

## PROPERTIES OF NANOMATERIALS ✓

The mechanical, electrical, optical, chemical, semiconducting and magnetic properties of nanomaterials depend on the grain size, and inter-particle separation.

## 7.3.1. Mechanical Properties

The Hall and Petch relation is given by,

$$\text{Yield strength } (\sigma_y) = \sigma_l + K d^{-1/2} \quad \dots (1)$$

where,  $\sigma_l$  is the lattice friction stress  
 $d$  is the average grain size, and  
 $K$  is the unpairing constant.

Similarly,

$$\text{Hardness } (H) = H_l + K d^{-1/2} \quad \dots (2)$$

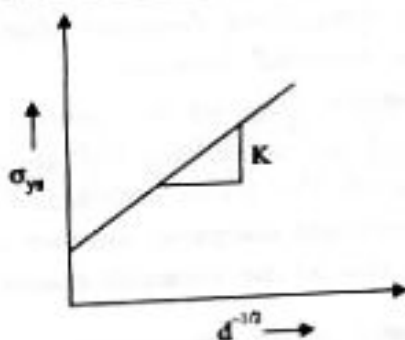


Fig. 7.13. Yield Strength Versus Grain Size

Relations (1) and (2) shows that if the grain size is decreased, strength of the material is increased. This is because the movement of dislocations is impeded by grain boundary. Hence, nano phase materials with exceptionally small grain size are found to be highly strong.

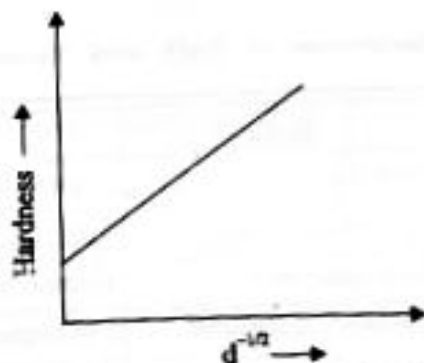


Fig. 7.14. Hardness Versus Grain Size



Fig. 7.14 shows the increase in hardness of 'Cu' because of decrease in grain size. Similarly, Fig. 7.15 shows the decrease in melting temperature when the grain size is reduced.

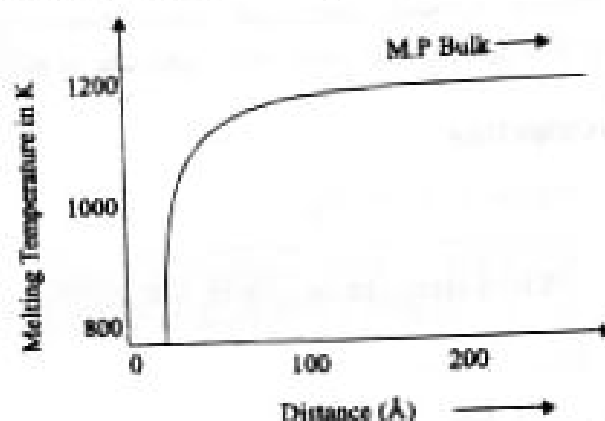


Fig. 7.15. Melting Point of Gold as a Function of Grain Size

### 7.3.2. Chemical Properties

Chemistry play an important role to create the as required nanoscale structure. When the particle size is reduced from the bulk, the electronic bond in the metals becomes narrow. It leads to the transformation of delocalized electronic states into more localized molecular bonds. As a result, the ionization potential increases.

The nanoscale particles exhibit some of the unusual behaviour such as equilibrium vapour pressure, chemical potential and solubilities that are higher than some material when they are expressed as large particles. The above information reveals that the high surface to volume ratio, the change in geometry and electronic structure changes the optical and electronic properties of nanoscale materials due to the chemical reactivity.

### 7.3.3. Magnetic Properties

The magnetic properties of nano particles in clusters differ from that of bulk material. This is given in Table 7.1. Even the clusters of non-magnetic solids are found to be magnetic, it has been found theoretically and experimentally that the magnetization exists in small sized particles and disappears in clusters containing more than 80 atoms. At small sizes, the clusters become spontaneously magnetic.

TABLE 7.1. Magnetism of Bulk and Nanophase Materials

Materials	Bulk	Clusters
Na, K	Paramagnetic	Ferromagnetic
Fe, Co, K	Ferromagnetic	Super paramagnetic
Gd, Tb	Ferromagnetic	Rotors/Super paramagnetic
Cr	Antiferromagnetic	Frustrated paramagnetic
Rh	Paramagnetic	Ferromagnetic



### 7.3.4. Electrical Properties

Electrical conductivity is defined by,

$$\text{Electrical conductivity } (\sigma) = \frac{Ne^2\tau}{m} \quad \dots (3)$$

where,

$N$  is number of electrons,

$e$  is electron charge,

$\tau$  is relaxation time,

$m$  is the mass of electron.

Resistivity is the inverse of conductivity. Resistivity in nanosized materials is in general larger than that in polycrystalline materials. The electrons get scattered at grain boundaries resulting into increase of resistance. Therefore, resistivity of nanosized materials is generally quite large.

### 7.3.5. Optical Properties

Spectral shift of optical absorption and fluorescence properties, increased quantum efficiency of semiconducting crystals are the optical properties of nanomaterials.

### 7.3.6. Bio-compatibility

Increased permeability through biological barriers like membranes, blood-brain barrier etc., improved the bio-compatibility of the nanomaterials.

### 7.3.7. Quantum Size Effect (QSE)

Nanosize particles absorb light and emit an appropriate colours. This is a size dependent property. For example, a semiconductor like CdS is normally reddish in colour at 6 nm size.

6 nm particles → Red

4 nm particles → Orange

3 nm particles → Yellow

2 nm particles → White

Not only the visual appearance but other properties also change dramatically. The mechanical, thermal, optical, magnetic, and other properties also changes at some size characteristic of that materials.

#### Examples

CdS and Gold.



## 7.4

## APPLICATIONS OF NANOMATERIALS

Nanoparticles are used in a variety of fields and devices such as electrical devices, memory devices, fuel cells, defense field, aero-space industry etc. In this section, we shall briefly discuss some of these applications.

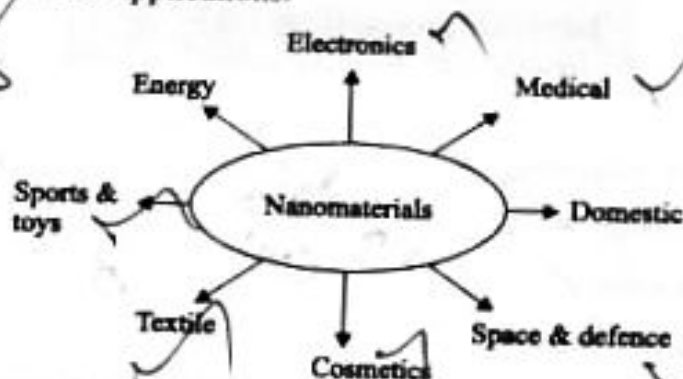


Fig. 7.16. Applications of Nanomaterials

## 1. Electrical and Electronic Devices

The nanoparticles are used for fabricating nano-transistors, multilayer capacitors, quantum computing and display technologies, noise filters and stabilizers. The advantages of these devices are low power loss and smaller in size.

**Examples**

$\text{BaTiO}_3$ ,  $\text{ZnO}$  etc. are used for current controlling devices such as thermistors.

## 2. Memory Devices

- (i) These are used to produce very tiny permanent magnets with high energy product value. The tiny magnets find applications in high density magnetic recording.
- (ii) Quantum well, quantum dots and quantum wires having quantum confinement are produced from semiconductor nanomaterials which are acting as computer storage materials with high density.
- (iii) The magnetic devices made of  $\text{Cu}$ ,  $\text{Fe}$  alloys are used in RAM, READ / WRITE heads and sensors.

## 3. Defense Industry

The nano particles are used in fuel cells and infrared windows which are effective in defense applications.

**Examples**

Nano Ceramic powders.

## 4. Additives and Pastes

Due to reduction in processing time, cost and higher productivity, the nano phase materials such as  $\text{BaTiO}_3$ ,  $\text{ZnO}$  etc., are used for additives and pastes which are used for screen printing.



## 5. Optical Devices

These materials are used for fabrication of semiconductor laser which is smaller in size. These lasers have high efficient compared to lasers made by conventional materials.

## 6. Cosmetics and Body Care Products

The nano ceramic powders such as  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$  etc. are used for cosmetic and body care products.

## 7. Communications

Miniaturized micro chip patch antenna which have large bandwidth are manufactured using nano-phase materials. The weight of this antenna is very much reduced compared to conventional ones.

## 8. Energy

Nanotechnology will play an important role in the field of energy.

- (i) Hydrogen is a good source of fuel for automobiles and other transportation purposes. Carbon nanotubes are used as Hydrogen storage material.
- (ii) Some metal hydride nanoparticles like Nickel hydrides and ultra light weight materials like Aerogels are found to be better options than the conventional materials in improved batteries.

## 9. Automobiles

- (i) Very powerful motors using nanoparticles like  $\text{Ni-Ti}$  alloys perform better and are less power hungry than other motors.
- (ii) By using nanoparticles clay, better, light weight, and less rubber consuming thinner tyres are possible.

## 10. Sports and Toys

- (i) Good quality tennis racquets are made from nano-carbon.
- (ii) Nanomaterials based motors are used by toy industry to make them very smooth and soft.

## 11. Textile

- (i) Special threads and dyes used in textile industry are the nanomaterials product. These clothes do not require ironing and frequent cleaning.
- (ii) Some companies used Silver nanoparticles in washing machine which will make clothes germ-free.

12. It is used in information storage, refrigeration, computers, and solar cells.

13. BIOMEMS are used in bio-fluidic chips for chemical and biochemical analysis in medical diagnostics and implantable pharmaceutical drug delivery.

14. Nanotube based biosensors are used for cancer diagnostics.

NEET



15. Nanomaterials are used as molecular switches, nanotube flat-panel displays, fast logic gates, and nanoscopic lasers.
16. Zeolite, a special nanomaterial is used by petroleum industry as catalysts.

## 7.5 CARBON NANOTUBES

### 1. Carbon Nanotubes

Carbon nanotubes can be considered as cylinders made of Graphite sheets, mostly closed at the ends, with Carbon atoms spread at the apexes of the hexagons, just like on a Graphite sheet. Thus, as shown in Fig. 7.17, one can consider Carbon nanotube as folding of a Graphite sheet. They are formed by rolling the Graphite sheet about an axis parallel to C - C bonds.

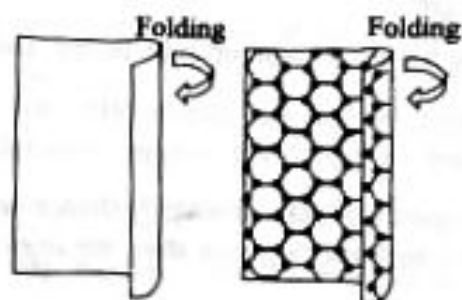


Fig. 7.17. Rolling the Carbon Sheet to Obtain Carbon Nanotube

### 2. Single and Multi Wall Nanotubes

It is also possible that many concentric cylinders may be formed as a nanotube called Multi Wall Carbon Nanotubes (MWCNT). The distance between their walls is  $\approx 0.334$  nm. MWCNT are most common and easily formed. However under certain conditions it is possible to obtain even Single Wall Carbon Nanotubes (SWCNT). Fig. 7.18 illustrates both SWCNT and MWCNT.

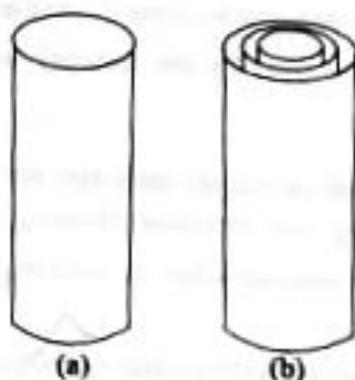


Fig. 7.18. (a) Single Wall (SW) (b) Multi Wall (MW) Tubes



3. As the magnetic properties of the metallic glasses are not affected by irradiation they are used in making containers for nuclear waste disposal.
4. These materials are used in the preparation of magnets for fusion reactors and magnets for levitated trains etc.
5. Metallic glasses can also be used for making watch cases to replace Ni and other metals which can cause allergic reactions.
6. The excellent corrosion resistance property makes these materials to be ideal for cutting and in making surgical instruments. In addition, they can be used as a prosthetic material for implantation in the human body.
7. In future, the usage of metallic glasses in the electronic field can yield; stronger, lighter and more easily moulded castings for personal electronic products.
8. Metallic glasses are used in tap reorders as heads, in manufacturing of springs and standard resistances.

## 14.7 Nanomaterials

Nanomaterials play a vital role in the recently developed science and technology.

*Nanomaterials are the materials containing nanocrystals i.e., their grain size is in the 1 to 100 nm range. The nanomaterials may be metals, alloys, intermetallics and ceramics.*

Conventional materials have grain size ranging from micron to several millimeters and contain several billion atoms each. But, nanomaterials contain only nine hundred atoms each. As the grain size decreases, there is a significant increase in the volume fraction at grain boundaries or interfaces.

In general, the nanomaterials exhibit greatly altered properties such as physical, chemical and mechanical compared to their normal large sized grain counterparts with the same chemical composition. Because of their unique microstructure, the nanomaterials are said to have high strength, hardness, formability, toughness and are more brittle.

## 14.8 Synthesis

Using a variety of synthesis methods, it is possible to produce nanostructured materials in the form of thin films, coatings, powders and as a bulk material.

The methods used for the synthesis of nanoparticles can be broadly classified into two types, namely physical and chemical methods.

The most commonly used techniques of nanomaterials preparation are explained in brief in this section.

1. Mechanical alloying.
2. Inert gas condensation.
3. Sol gel technique.

### 1. Mechanical alloying

It is a solid state material processing technique in which the materials can be synthesised even at room temperature. This technique is also used to produce metastable structures. Ultrafine nanomaterial with high homogeneity is prepared by this technique. Since, the starting material is powder this technique is of low cost but of high efficiency.



## 2. Inert gas condensation

In this technique, the base material is evaporated and the evaporation is allowed to pass through a chamber filled with inert gases like argon or nitrogen. When the evaporated atoms come into contact with the inert gas they get condensed into spherical particles. Process parameters can be used to control the size of particles.

## 3. Sol gel Technique

In this technique, nitrates or carbonates are taken as pre cursors which are dissolved in deionized water. The solution is kept at a suitable temperature and some amount of gelling agents are added to it. Thus, the viscosity, temperature and PH of the solution is controlled in this technique. The nanomaterials in the form of thin film coatings are made by this technique.

For thin film coating, substrates like copper, nickel or glass are taken and dipped in the solution before gel formation. Finally, annealing has to be done to get thin film.

Of the three; the sol gel synthesis is most widely used due to the following reasons.

1. In this technique, materials; both ceramic and metals can be produced at ultra low temperature.
2. Any type of material can be synthesised in large quantities very cheaply.
3. Extremely homogeneous alloys and composites can be produced.
4. High purity (99.9999%) in synthesised materials can be obtained.
5. In this technique, the microstructure and physical, chemical and mechanical properties of the final products can be controlled.
6. Co-synthesize of two or more materials simultaneously is possible.

## 14.9 Properties

1. The nanomaterials have high strength, hardness, formability and toughness.
2. These materials are more brittle.
3. These materials exhibit super plasticity (i.e., undergoing large deformation without necking or fracture) even at lower temperatures.
4. Magnetic moment of nanomaterials can be increased by decreasing the particle size.
5. Optical density of these materials can be varied with the diameter.
6. Size of the grains controls the mechanical, electrical, optical, chemical, semiconducting and magnetic properties.
7. The melting point of nanomaterials gets reduced on reducing the grain size.
8. The magnetisation and coercivity are higher.

## 14.10 Applications

1. Nanomaterials are used for the fabrication of signal processing elements such as filters, delay lines, switches etc.
2. Using these materials, soft and permanent magnets can be manufactured which is said to have a wider application.
3. Nanocrystalline materials like tungsten carbide, tantalum carbide and titanium carbide are used in making cutting tools. These tools are much harder and lasts longer than their conventional (large grained) counter parts.



4. These materials are used to make semiconductor lasers, nanotransistors, memory devices such as recording heads and magnetic storage devices etc.
5. Hydrogen based sensors made by nanomaterials are used in power generation.
6. Nanomaterials are used for the manufacturing of small size, light weight microstrip patch antennas. These miniaturized antennas are said to have large bandwidth, tunability and mechanical flexibility.
7. These materials are used in enzyme removal of  $\text{CO}_2$  from air and waste water treatment.
8. Nanocrystalline  $\text{ZnO}$  thermistors are used in current controlling devices.
9.  $\text{SiC}$  nanocrystalline is used in making artificial heart valves due to its low weight, high strength, inertness, extreme hardness and wear resistance.
10. When nanocrystalline ceramics such as zirconia and alumina are used as liners in automobile engine cylinders, they help in retaining heat much more efficiently and result in complete and efficient combustion of the fuel.

The application of nanomaterials are not limited only to the above mentioned; still, there are a large number of applications and uses of it.

## SHAPE MEMORY ALLOYS

### 14.11 Introduction—Smart Materials

The trend towards developing better and improved functional materials has resulted in the new engineering functional materials which are referred to as *smart or intelligent materials*.

The smart materials mimic biological functions viz., sensing, actuation and control. These materials can respond to external stimuli such as, temperature, pressure, optical, electric field, moisture, magnetic field and so on.

These smart characteristics offers numerous possible applications for these materials in aerospace, medical engineering, automobile engineering, civil infrastructure and consumer electronics.

Among several smart materials, Shape Memory Alloys (SMA's), piezo electric materials and fiber optic sensors are currently receiving wide attention.

### 14.12 Shape Memory Alloys (SMA)

Shape memory alloys (SMA's) are metals which exhibit two very unique properties, Shape Memory Effect (SME) and pseudo elasticity or Super Elasticity (SE).

These alloys are a unique class of materials, which remember their shape even after severe deformation. i.e., when a SMA is once deformed in the cold shape (martensite) these materials will stay deformed until heated; where, upon heating they will spontaneously return to their original pre-determined hot shape (austenite).

It is observed that, the structural changes at the atomic level contributes to this unique properties of the materials.