#### Unit IV-Nanotechnology

#### Nanotechnology:

Nanotechnology is defined as the design, characterization, production and application of structures and system by controlling shape and size at nanometer scale.

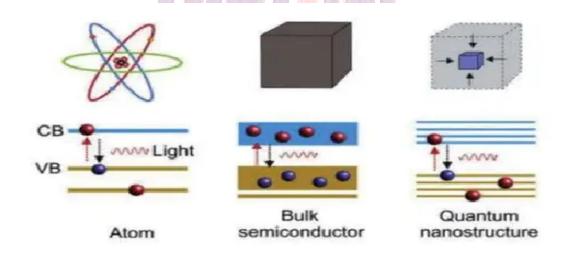
- NANOSCALE: A nano means  $10^{-9}$ . A nanometer (nm) is one thousand million TH of a meter ( $10^{-9}$ ) i.e., 1 nm = 1/1,000,000,000 m or  $10^{-9}$  m
- NANO MATERIALS: Nanomaterials are defined as those materials which have structured with size between 1 to 100nm.
- NANOSCIENCE: Nano science is the study of the fundamental principles of molecules and structure having size with in the of range of nano scale.

The two factors that nano properties are changes they are,

- i). Quantum confinement effect
- ii). Increase in surface to volume ratio

#### **QUANTUM CONFINEMENT EFFECT:**

- According to band theory, solid materials have energy bands and isolated atoms possess discrete energy levels.
- Nanomaterials are in intermediate to the above two cases.
- For nanomaterials, if the dimensions of potential wells or potential boxes are of the order of the de Broglie wavelength of electrons (mean free path of electrons), then the energy levels of electrons change, and the electron will remain confined to a small region of the material. This is called **quantum confinement.**
- Energy is discrete, not continuous in a quantum system.
- This effect, can changes the optical, electrical and magnetic behavior of materials of nano particles.



- As the materials reduced to nanoscale can suddenly show very different properties compared to what they exhibit on a bulk. For examples, Opaque substances become transparent (Copper)
- Different sized nanoparticles scatter different wavelengths of light incident on it and hence, they appear with different colours.
- Inert materials become catalysts (Platinum).
- Stable materials become combustible (Aluminum).
- Insulators become conductors (Si).
- Solids turn into liquids at room temperature Gold)

**SURFACE TO VOLUME RATIO:** When bulk particles become nano sizes the surface to volume ratio increases. For this let us consider a sphere of radius 'r'.

# $\frac{\text{Suraface area of sphere}}{\text{Volume of the sphere}} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{12\pi r^2}{4\pi r^3} = \frac{3}{r^3}$

Thus when the radius of the sphere decreases, its surface volume ratio increases.

Let us consider another example, as shown in figure .

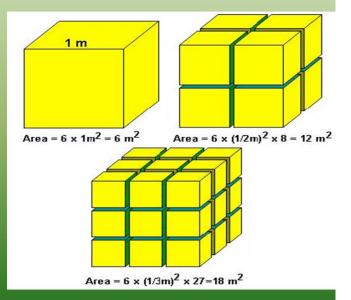
For one cube the surface area  $=6m^2$ 

When I divided into 8 pieces the

surface area=  $12 {
m m}^2$ 

When I divided into 27 pieces the surface

area= 
$$27m^2$$



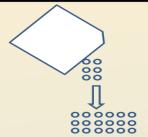
- ➤ Thus, we find that when the given volume is divided into smaller pieces, hence the surface particle size decreases.

  So we are coming to following conclusions:
- > Nano particles are very small in size.
- Very high surface area to volume ratio.
- In nano materials a large number of atoms will present on the surface.
- > Its makes materials more chemically reactive which leads to changes of their properties.

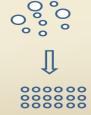
## **FABRICATION OF NANO - MATERILAS**

Nano materials can be fabricated in any two ways they are.

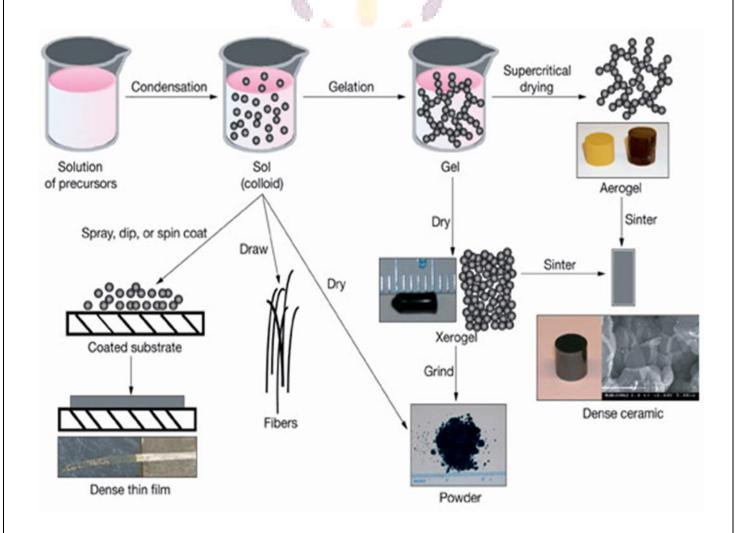
(i). Top down approach, in which bulk materials are reduced into nano sizes as shown in figure



(ii).Bottom up approach, in which nano materials are made by building atom by atom as shown in below figure,



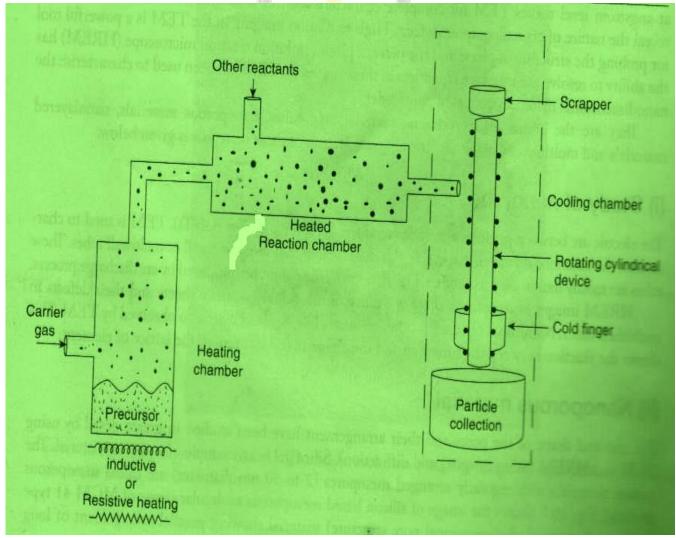
**SOL-GEL METHOD**: This method is Bottom-up fabrication method



- In solutions, nanosized molecules are dispersed randomly whereas in colloids, the molecules have diameters in the range of 20µm-100µm and are suspended in the solvent. So, the colloid appears cloudy.
- A colloid that is suspended in a liquid is called a **Sol**. The gelation of the sol in the liquid to form a network is called **gel**. Gel is the suspension that keeps its shape.
- Sol-gel formation occurs in different stages
  - a). Hydrolysis
  - b). Condensation and polymerization of monomers to form particles.
  - c). Agglomeration of particles.
  - This is followed by the formation of networks which extends throughout the liquid medium and forms a gel.
- Using sol-gel method, silica gels, zirconia and yttrium gels and aluminosilicate gels are formed.
- Nanostructured surfaces are formed using the sol –gel method

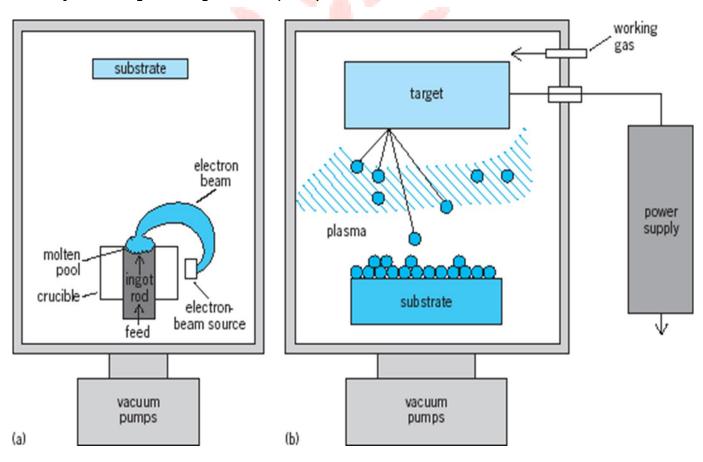
# CHEMICAL VAPOUR DEPOSITION METHOD(CVD):

1). This method is used for prepare nano powders and this method is top-down fabrication method.



- 2). As shown in figure the apparatus consists of
  - (a) Heating chamber
  - (b) Reaction chamber
  - (c) Cooling chamber
- 3). In this method the material is heated to form a gas and is allowed to deposit on a solid surface.
- 4). A metal organic precursor is taken into heating chamber and heated to high temperature so that it can be melted and evaporated.
- 5). Inert gas like He or Ne can be introduced into the heating chamber this acts as a carrier gas and carries the precursor vapour to reaction chamber. Inside reaction chamber other Reactants are added
- 6). Some other reactants are introduced into reaction chamber to control reaction rate and the hot precursor atoms/Molecules collide with the cold reactance atoms/molecules through nucleation and form small clusters (nano particles).
- 7). Then the clusters from reaction chamber is passed into cooling chamber. Liquid nitrogen is used for cooling this chamber.
- 8). The cooling chamber contains a rotating cylindrical device on a cold finger as shown in figure. The nano particles(clusters) are allowed to condense on the rotating cylindrical device and scraper is used to collecting the nano particles.

# Physical Vapour Deposition (PVD):



## Various methods of PVD

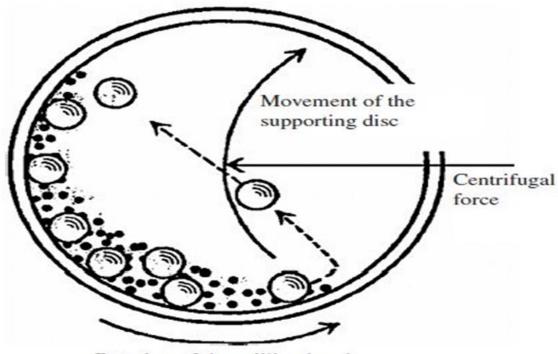
- **Evaporative deposition:** The material to be deposited on the mounted substrate within the vacuum chamber is heated and vaporized by electrically resistive heating. Condensation of the vaporized material takes place and by proper control, atomic layer deposition can be obtained.
- **Electron beam physical vapour deposition:** The material to be deposited is heated to a high vapour pressure by electron bombardment in high vacuum.
- **Sputter deposition:** The material to be deposited is vaporized by bombarding the material with a glow plasma discharge. The plasma is usually confined and localized around the target, by a magnet.
- **Cathodic arc deposition:** In this a high-power arc is directed at the target material, that blasts away some of the material into vapour.
- **Pulsed laser deposition:** In this high-power pulsed laser ablates the material from the target into a vapour.

In all these methods, the material is converted into vapour phase, for further deposition on the substrate.

# Ball Milling:

- This is a **top-down technique**, producing very small structures from larger pieces of the material.
- In this method, small balls of the material are made to rotate inside a drum and drop under the influence of gravity, onto a solid present in the drum. The solid is broken into nanocrystallites.
- This is also known as mechanical crushing. This method is used for a large number of elements and nano oxides. For example, Iron nanoparticles of 13-30 nm can be formed.

#### Horizontal section



Rotation of the milling bowl

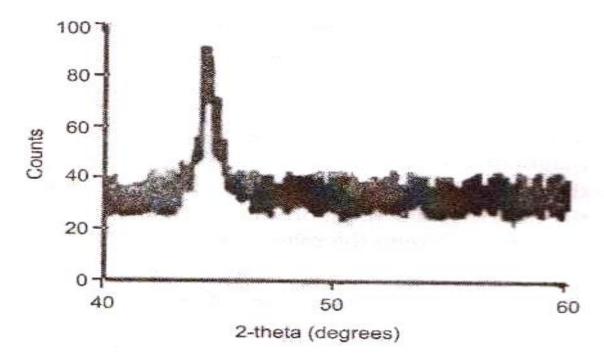
## X-ray Diffraction Method:

- Phase identification using X-ray diffraction lies mainly on the position of the peaks in the diffraction profile and to some extent on the relative intensities of these peaks.
- The shape, particularly the width of the peak is a measure of the amplitude of thermal vibrations of the atoms at their regular lattice sites.
- It can also be a measure of any deviations from the normal structure. Ex: Plastic deformation, impurity doping, second phase addition to the host phase.

When X-ray powder pattern is taken on poly crystalline powders, the crystallite size causes peak broadening. The crystallite size is easily calculated as a function of peak width, specified as Full Width at Half Maximum (FWHM), peak position and wavelength. The average crystallite size 'L' is given by,

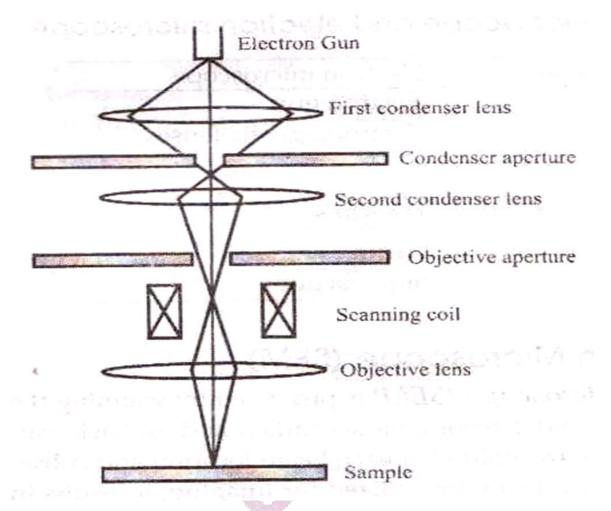
$$\langle L \rangle = \frac{K\lambda}{B_{1/2}cos\theta_B}$$

Where,  $\theta$  is the Bragg's angle B is FWHM of the diffraction peak; K is a constant and  $\lambda$  is the wavelength of X-rays used.



# Scanning Electron Microscopy (SEM)

The image in scanning electron microscope is produced by scanning the sample with a focused electron beam and detecting the secondary and back scattered electrons. Electrons and photons are emitted at each beam location and subsequently detected.



## Schematic representation of SEM

- The electron gun produces a stream of monochromatic electrons.
- The electron stream is condensed by the first condenser lens. It works in conjunction with the condenser aperture to eliminate the high angle electrons from the beam.
- The second condenser lens forms the electrons into a thin, light coherent beam.
- Objective aperture further eliminates high angle electrons from the beam.
- A set of coils acting as electrostatic lens scans and sweeps the beam in a grid fashion (as in television)
- The objective lens focuses the scanning beam onto the part of the specimen.
- When the beam strikes the sample, interaction occurs. The intensity of display is determined by the interaction number. More interactions give a brighter pixel.
- This process is repeated until the grid scan is finished and then repeated. The entire pattern can be scanned 30 times per second.

#### SEM gives useful information on

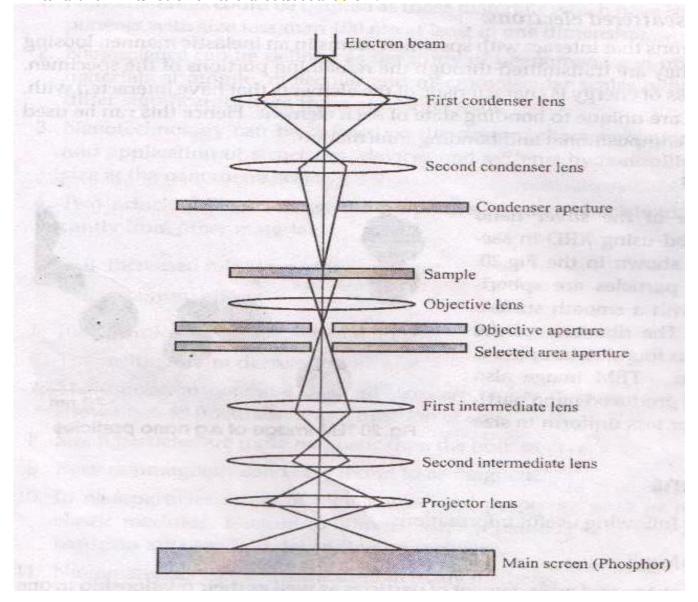
• **Topography:** The surface features of an object or "how it looks," its texture, detectable features, limited to a few nanometers.

- **Morphology:** The shape, size and arrangement of particles making up the object that are lying on the surface of the sample or have been exposed by grinding or chemical etching, detectable features limited to a few nanometers.
- **Composition:** The elements and compounds the sample is composed of and their relative ratios, in areas approximately 1 micrometer in diameter.
- **Crystallographic Information:** The arrangement of atoms in the specimen and their degree of order, only useful on single-crystal particles >20 µms.

# Transmission electron microscope (TEM):

Transmission electron microscope (TEM) is an instrument for complete characterization of nanoscale microstructure materials or complete study of nano particles.

A schematic representation TEM is shown in figure. Each part is labelled and their functions are discussed below.



- 1). The electron gun produces a stream of monochromatic electrons.
- 2). This stream is focused to a small coherent beam by the first and second condenser lenses.
- 3). The condenser aperture knocks off high angle electrons.
- 4). The beam strikes the specimen.
- 5). The transmitted portion is focused by the objective lens into an image.
- 6). Objective aperture enhances the contract by blocking out high angle diffracted electrons
- 7). Selected area aperture enables to examine the periodic diffraction of electrons by an ordered of atoms in the sample.
- 8). Intermediate and projector lenses enlarge the image
- 9). The beam strikes the phosphor screen and image is formed on the screen. The darker areas of the image represent thicker sample areas since these areas transmit lesser electrons. The brighter areas of the image represent thinner sample areas since these areas transmit more electrons.

## TEM gives the information about,

- 1) **Morphology:** The size, Shape and arrangement of particles as well as their relationship to one another on the scale of atomic diameters.
- 2) Crystallographic information: The arrangement of atoms in the specimen and their degree of order, detection of atomic scale defects, a few nanometers in diameter.
- 3) Compositional information: The elements and compounds, the sample is composed of and their relative ratios.

#### APPLICATIONS OF NANO TECHNOLOGY:

Though nano particles are very small, they the important materials to build the future world. They have applications almost in all engineering fields as follows few of applications are given below,

- 1). Since they are stronger , lighter so they are used to make hard metals.
- 2). Cutting tools made of nanocrystalline materials.
- 3). It is possible to produce unusual colours paints using nano particles.
- 4). Nano sized titanium dioxide and zinc oxide are currently used in sun screens.
- 5). These materials are used to store the information in smaller chips.
- 6). Nano-materials are used to make CD's and semiconductor laser.
- 7). They are used in mobiles, laptops etc.
- 8). Nanotechnology includes fabrication of nano wires used in semiconductors.
- 9). Recently nano-robots were designed, which were used to remove the damaged cancer cells and also modify the neuron network in human body. 10)They are used in hydrogen storage devices.