Module 6: NANOTECHNOLOGY

Syllabus:
Nanomaterials: Properties (Optical, electrical, magnetic, structural, mechanical) and applications
Surface to volume ratio
Two main approaches in nanotechnology - Bottom up technique and Top down technique
Tools for characterization of nanoparticles: Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Atomic Force Microscope (AFM),
Method to synthesize nanomaterials: Ball milling, Sputtering, Vapour deposition, Solgel

Nanomaterials

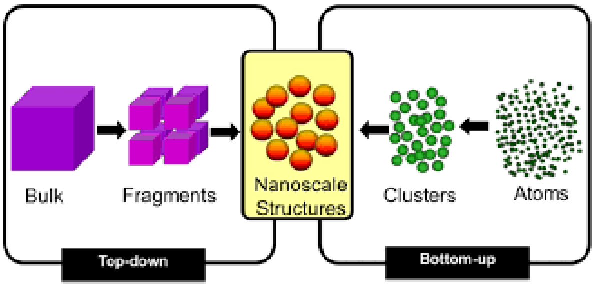
Nanomaterials is defined as those materials which have structured components with size less than 100nm atleast in one dimension.

e.g Fullerenes, Carbon nanotubes (CNT), Quantum dots etc.

The technology emerged out from nanomaterials (0.1-100nm) is called nanotechnology. **Nanotechnology** can be defined as the design, characterisation, production and application of structures, devices and systems by controlling size and shape at the nanometer scale.

Two approaches in nanotechnology

There are two approaches for synthesis of nanomaterials and development of nanostructures



(1) Bottom up approach

In this nanomaterials are made by building atom by atom, molecule by molecule, cluster by cluster from the bottom. Molecular components arrange themselves into some useful conformation using the concept of molecular self assembly.

e.g: Synthesis of nanoparticle by colloid dispersion (sol- gel process)

(2) Top down approach

In this a bulk material is broken or reduced in size or pattern. The developments of microelectronics is based on this approach.

E.g.: Synthesis of nanoparticles by ball milling method.

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Properties of nanomaterials

The properties of materials drastically changes at nanoscale due to two reasons, increase in relative surface area, and quantum effects.

Optical: The optical properties of nanomaterials are highly dependent on size and shape of nanomaterials (for e.g., gold at 5 nm diameter appears red in colour). Spectral shift of optical absorption and fluorescence properties occurs at nanoscale in comparison with bulk form. Increased quantum efficiency of semiconductor crystals, Surface Plasmon Resonance (SPR) in metal nanoparticle are interesting properties of nanomaterials

Electrical: Reduction in particle size changes the electric properties of nanomaterials. The presence of even a minute quantity of nanomaterials in composites modulates the electrical parameters like reduction in resistivity and increase in conductivity, dielectric constant etc., which are useful for several technological applications. For example the display performance of liquid crystal composites is much improved in the presence of nanomaterials

Magnetic: Nano sized materials are more magnetic than their bulk form, which includes increased magnetic coercivity, superparamagnetic behaviour etc. The nanoparticles have large surface to volume ratio. At the surface, the symmetry and lattice constant change. Due to this. some materials show ferromagnetic behaviour which are non-ferromagnetic in bulk form.

Structural: The structure of nanoparticles is entirely different from their bulk form. Reducing the particle size lead to increase in surface to volume ratio. Lattice parameter and interatomic spacing vary, when it changes to nano form. Bonds, bond strength, surface morphology defect structures in nanomaterials is entirely different.

Mechanical: Mechanical properties of nanomaterials increase with decreases in size, because smaller the size lesser is the probability of finding imperfections (such as dislocations, vacancies etc.). The hardness and yield strength of nanomaterials improves significantly due to perfect defect free surface. Elastic modulus and toughness also increased at nanoscale.

Applications of nanomaterials

1) Electronic applications:

(i) Due to shrinking of sizes of electronic equipments, electronic miniaturization is possible

(ii)It is possible to manufacture some devices which are faster, compact and relatively cheaper.

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2) Automobile Applications

(i) Nanotube composites have better mechanical strength than steel

(ii)Nanoparticle paint provide smooth thin coating

(iii) The higher quality tyres can be manufactured using nanoparticles.

3) Medical

(i) Nanotechnology is used in drug delivery effectively

(ii) Nanotechnology is used in the effective detection of cancer or tumours.

4) Textiles

(i) It is used in manufacturing of clothes which would give pleasant look and high comfort

(ii)Nanotechnology is used in the manufacturing of special threads and dyes

5) Environmental

(i) It is used in sensors which are useful in water purification, pesticides etc.

(ii)Use of nanoparticles as hydrogen storage reduces pollution due to vehicles.

Surface to volume ratio

Increased surface area or increased surface to volume ratio is one of the most important factor which changes the properties of nanomaterials.

Let us consider a sphere of radius ‘r’

Its surface area $S = 4\pi r^2$

Its volume $V = \frac{4}{3}\pi r^3$

Surface area to volume ratio (S/V) $= \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$ $\quad (\propto \frac{1}{r})$

When the radius of the sphere decreases, its surface to volume ratio increases. The more the S/V ratio, the greater is the efficiency of nanomaterial. This makes nanomaterial more reactive

For example: For a cube with side a; $S/V = \frac{6a^2}{a^3} = \frac{6}{a}$ = 3 if a=2

For a sphere S/V = 1.5 if radius r = 2

Hence cube with larger S/V ratio than sphere is more efficient

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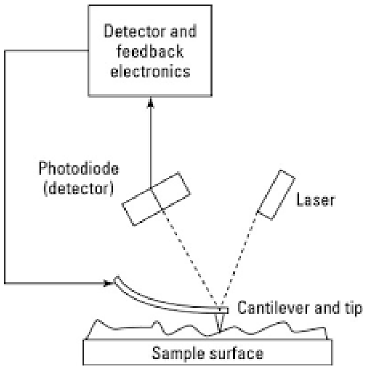
Tools for characterization of nanoparticles:

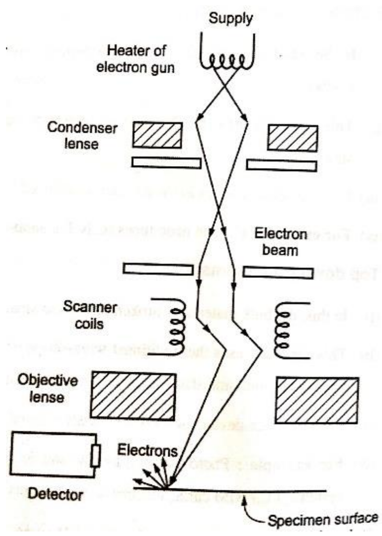
(1) Atomic Force Microscope (AFM)



The AFM consists of a cantilever with a sharp tip (probe)at its end which is used to scan over a sample surface. As the tip approaches the sample surface, the tip experiences a force (repulsive or attractive). These force between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. During scanning, the tip will have vertical movements which depend upon the topography (i.e. nature) of the sample.

A laser is positioned such that its light strikes at an oblique angle at the end of the cantilever. The vertical movement of the tip is recorded using laser beam and is reflected onto photodiode. A plot of laser deflection versus tip position on the sample surface provides the resolution of hills and valleys that constitute the topography of sample surface. By using a feedback loop to control the height of the tip above. As AFM does not generate any current, hence both conducting and non conducting sample can be scanned.

(2) Scanning Electron Microscope (SEM)



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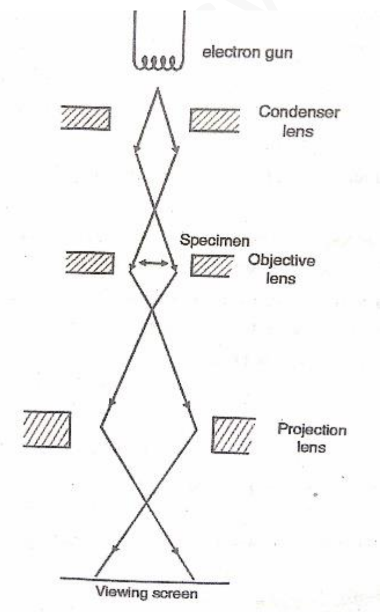
Here electron beam is obtained from electron gun (by heating of metallic filament). It is made to pass through condenser lens. Next stage is scanning of coil which is used to focus the electron beam on a small spot on specimen surface and also to scan surface (like electron beam scans in TV picture mode). When the electron hits the surface of specimen, other electron (secondary or backscattered electrons) will be scattered. Scattering of electron beam is because of the atoms on the surface of specimen, and these atoms have different scattering power. The scattered beam will form the image signals.

During the scanning of atoms by electron beam, the scattered electron intensities are measured by a detector and then displayed on the screen. For high scattering (that is scattering from heavy elements) the respective point on the viewing screen will be bright and for low scattering, the corresponding point on the screen will be dark. This develops required contrast for a clear image of the specimen. The SEM image is a 2D image map

Specimen as small as $50A^o$ size may be clearly resolved by SEM.

(3) Transmission Electron Microscope (TEM)



TEM is the most advanced microscope working on the concept of quantum mechanics. The TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Electrons of very high energy are used which passes through a series of magnetic lenses. The various components of TEM are : electron beam source i.e. electron gun, condenser lens, objective lens and fluoresecent screen. These lenses are electromagnetic whose focal lengths are varied to obtain optimized images.

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The source of electrons will provide a flow of electrons whose energy and hence wavelength can be varied ($\lambda = \frac{h}{\sqrt{2mE}}$) That is with increase in energy, wavelength can be reduced. This brings in higher resolving power and hence better magnification (nearly 1000 times that of optical microscope). The entire arrangement is placed in high vacuum to avoid extraneous scattering and absorption of electrons by air. The lenses are magnetic lenses and the magnified image is projected on a **fluorescent** screen.

A TEM specimen must be thin enough to transmit sufficient electrons to form an image with minimum energy loss. Therefore specimen preparation is an important aspect of the TEM analysis.

The main difference between SEM and TEM is that SEM creates an image by detecting reflected or knocked-off electrons while TEM uses transmitted electrons (electrons which are passing through the sample) to create an image. As a result, TEM offers valuable information on the inner structure of the sample, such as crystal structure, morphology and stress state information, while SEM provides information on the sample's surface and its composition.

Method to synthesize nanomaterials

1) Ball milling
2) Solgel
3) Sputtering
4) Vapour deposition

(1) Ball milling

Ball milling is a mechanical technique using top-down approach. The ball milling equipment consists of a hollow cylindrical shell having either horizontal or tilted axis about which it is rotated at very high speed. It is partially filled with hardened stainless steel or ceramic balls known as milling balls. The material to be crushed is added in the form of powder. They are allowed to rotate in circular paths and also about central axis and hence it is called a planetary ball mill (since it resembles the earths planetary motion). When continuously operated, the shell rotates, which lifts the balls up and drops them from the top of the shell. That is, the powder mixture is subjected to high energy collision from the balls. This lead to grinding of course particles to fine powder inside. The size of steel ball used in milling is inversely proportional to size of nanoparticles they produce. This method is used to make nanoparticles of metals and alloys.

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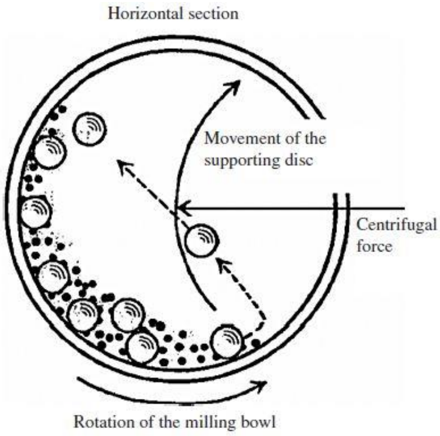
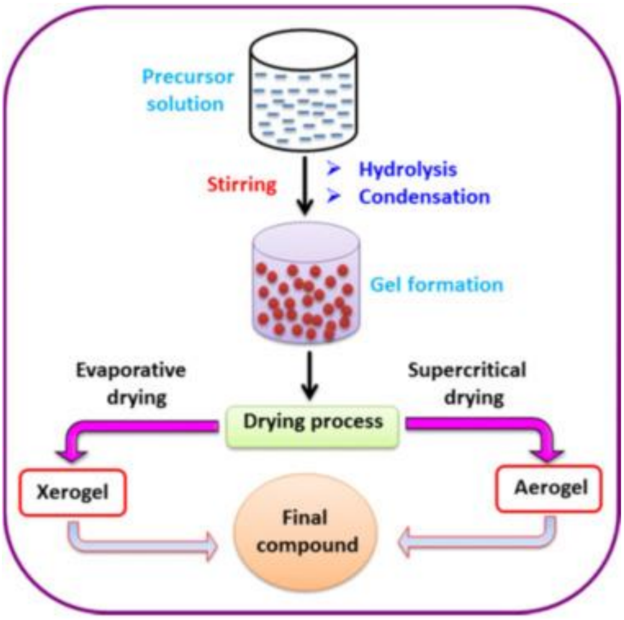


(2) Sol-gel process



Sol-gel process is a bottom –up approach technique. A sol is a solution with particles, suspended in it. When the particles in the sol- forms long polymers (chains) that span the entire sol, a gel is formed. In this process a colloidal suspension (sol) of the particles of metal compound is prepared first and then converted into gel. The sol/ gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

The sol-gel formation occurs in four stages

(i) Hydrolysis

(ii) Condensation

(iii) Growth of particles

(iv) Agglomeration of particles

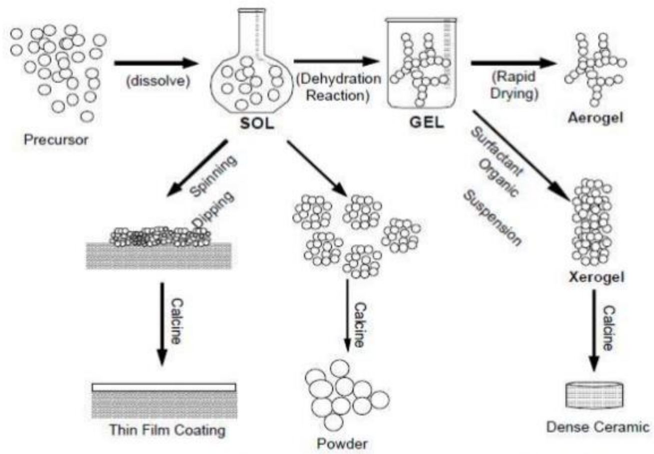
Step 1: A stable solution of alkoxide or solvated metal precursor (sol) is formed

Step 2: An oxide or alcohol bridged network (gel) forms by polycondensation

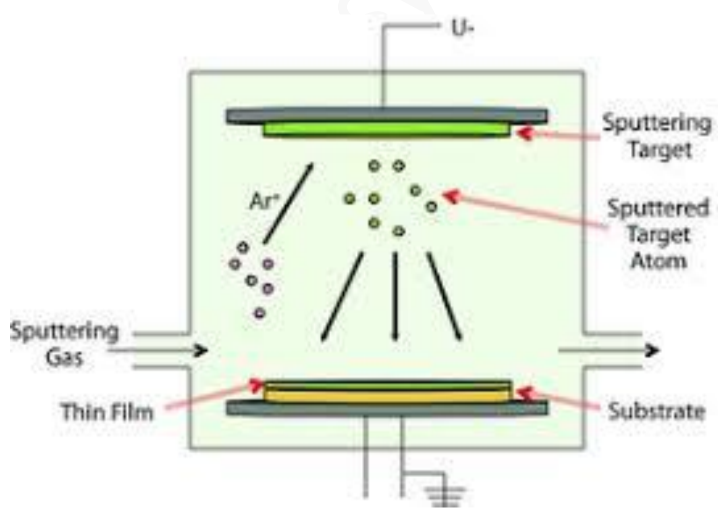
Step 3: The polycondensation reaction continue until the gel transforms into a solid mass, accompanied by contraction of gel network, and expulsion of solvent from gel process.

Step 4: Drying of the gel to remove water and other volatile liquids from gel. If the solvent is extracted under supercritical conditions, the product is an aerogel. If removal of solvent is by thermal evaporation, the resulting product is termed as Xerogel.

Step 5: Calcining the xerogel at temperatures up to 800^0C stabilizes the gel



(3) Sputtering



Sputtering is a technique to obtain thin films. In this technology particles are ejected from a solid target material by bombarding it with another high energetic particles. The substrate is placed in a vacuum chamber with source material, named target and an inert gas such as argon is introduced at low pressure. Using an RF (Radio Frequency) power source, gas plasma is struck, which result the gas to become ionized. The ions are accelerated towards the surface of the target, causing atoms of the source material to break from the target in vapour form and condense and get deposited on it resulting into a thin film. The film thickness can be controlled by varying the argon gas pressure and the time of sputtering process

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(4) Vapour Deposition

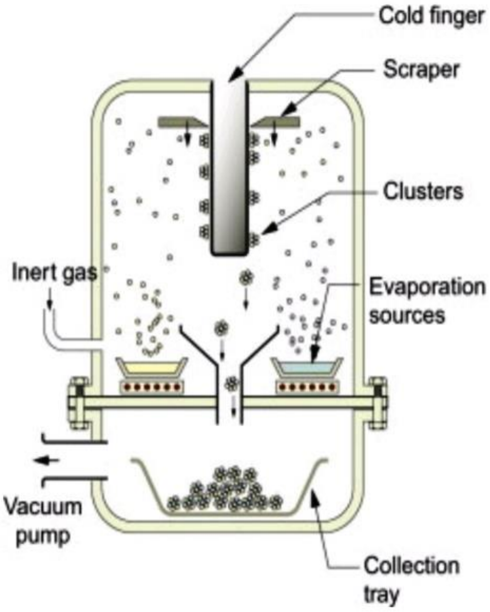
There are two categories (1) Physical Vapour Deposition (PVD) and (2) Chemical Vapour Deposition (CVD)

(a) Physical Vapour Deposition (PVD)

It is also called vacuum deposition or vacuum evaporation. The substrate is placed inside a vacuum chamber, in which source of material is also located. The source of material is then heated to the point where its starts to boil and evaporate. The evaporated molecules subsequently condense on all surfaces. The method used to heat (evaporate) the source material are

(i) **Resistive evaporation** – The material to be deposited is taken in a crucible around which a high resistance wire is wrapped. When a current is passed through the wire, it heats up the material and vapourizes it.

(ii) **e - beam evaporation**: - In e-beam evaporation, an electron beam is aimed at the source material causing local heating and evaporation.



This assembly is placed in an evacuated chamber. The evaporated particles get condensed and are collected on the cold finger (a rotating cylinder cooled with liquid nitrogen). The nanoparticles are removed from the surface of cylinder by means of a scrapper (in the form of a metallic plate) and then fall into the collection tray from funnel

(b) Chemical Vapour Deposition (CVD)

In this process, a solid is deposited on a heated surface via a chemical reaction from the gas or vapour phase. CVD reaction are carried out at very high temperature of 1500°C.

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