*Nanotechnology.

* Defination

- A branch of technology that deals with dimensions of less than 100 nm, especially manipulation of individual atoms.

→ The principle of nanoscale science and engineering refers to the fundamental understanding and technological advances from exploitation of new physical, chemical, electrical and biological properties of systems having size between molecules and bulk materials.

* Reasons of change in properties at Nanoscale :-

→ Surface area to volume ratio :- This value is very large for nanomaterials. If we consider a spherical material of radius 'r', then

$$\frac{\text{Surface area}}{\text{Volume}} = \frac{4\pi r^2}{4/3\,\pi r^3} = \boxed{\frac{3}{r}}$$

As the size of sphere decreases, the above ratio increases.

Hence nanomaterials possess large value of surface area as compared to its volume which is unlike that of bulk materials.

→ Quantum Confinement effects

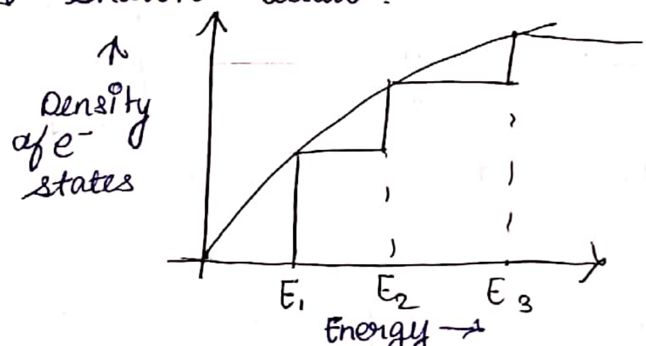
Acc. to band theory, solid materials have energy bands and isolated atoms possess discrete energy levels.

For nanomaterials, if the dimensions of potential wells or potential boxes are of order of de-broglie wave-length of e^- or mean free path of e^-, then energy levels of e^- will be confined to a small region of e^-. This is known as quantum confinement.

- The e^-s in bulk solid material possess alternatively discrete allowed and forbidden band of energies.
- As material changes from bulk to nanoparticle size, the energies of e^- change.
- A graph plotted b/w density of e^- state versus energies of e^- for bulk material is a parabola which is not the case of nanoparticle materials
- The quantum effects dominate at nanoscale
- They are zero, one and two dimensional nanoparticles

* Concept of quantum well, quantum wire and quantum dots

Quantum film (well) :- When one of the dimensions is reduced to nanometer scale, it is known as quantum film.
The graph b/w density of e^- states and energy is a step f^n as shown below.



$$D(E)dE = \frac{m^*}{\pi h^2} \Sigma H(E-E_i)dE$$

{m^* → effective mass of e^-}.

$H(E-E_i)$ is a step f^n called the 'Heaviside' f^n. The value is 0 for $E < E_i$ and 1 for $E \geq E_i$
The locus of all the corners of step f^n is a parabola.
Quantum wire :- The density of peaks are high @ energy value E_1, E_2, E_3 and decrease rapidly in between.

$$\Omega(E)\,dE = \frac{\sqrt{2m}}{\pi h} \Sigma \left| \frac{n_i H(E-E_i)}{\sqrt{E-E_i}} \right| dE$$

n_i → degeneracy factor $H(E-E_i)$ → Heaviside f^n.

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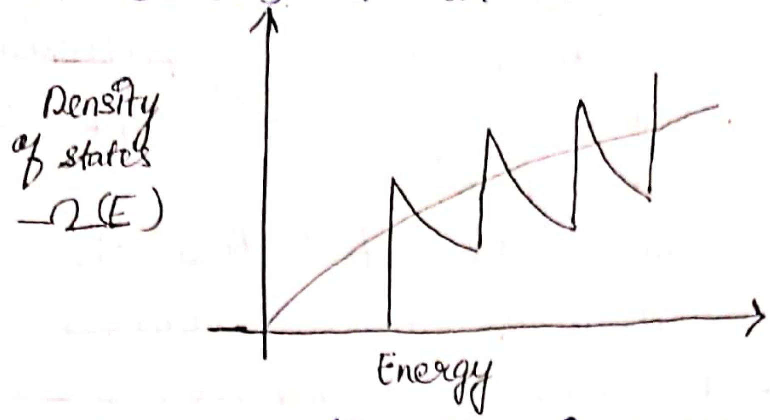
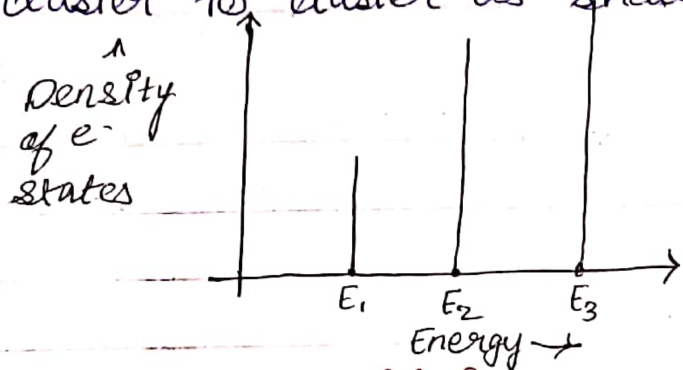
The density of states is of order 10^{-1}/MeV

[When 2 dimensions of a bulk material are reduced to nanometer scale, it is known as quantum wire]



Quantum dot :- When all 3 dimensions are reduced to nanometer scale, it is known as quantum dot. The energies of e^- in quantum dot appear as clusters. The density of e^- states vary from cluster to cluster as shown below.



* Diagnosis of nanomaterials :-

⇒ Scanning Tunnelling Microscope :-

How it works?

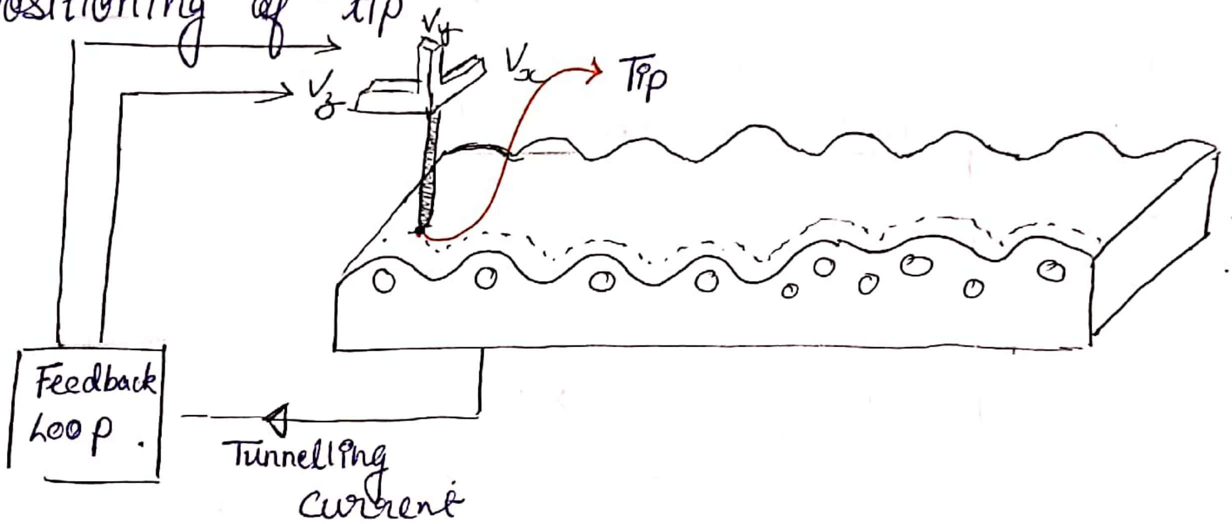
- The scanning tunneling microscope (STM) works by scanning a very sharp metal wire tip over a surface. By bringing the tip very close to the surface and by applying electrical voltage to the tip or the sample, we can image the surface @ an extremely small scall scale - down to resolving individual atoms.

STM is based on several principles.

→ Quantum Tunneling :- It is a quantum mechanical effect that occurs when e^- move through a barrier that the classically shouldn't be able to move through. As e^- have wave like properties, these waves do not end abruptly at a barrier, but taper off quickly (exponentially). If the barrier is thin enough, the probability f^n, through a barrier, may extend into next region. B'coz of sharp decay of probability f^n through a barrier, the no. of e⁻s that appear on the other side is much dependent on the barrier.

→ Piezoelectric effect - It is the effect that allows us to precisely scan the tip with angstrom level control.

Lastly a feedback loop is required, which monitors the tunnelling current and co-ordinates current and positioning of tip



* Scanning Electron Microscope.

→ Scanning electron Microscope (SEM) uses a focused electron probe to extract structural and chemical information point by point for a region of interest in a sample.

→ It is a type of e^- microscope that images a sample by scanning it with a high energy beam of electrons in a raster scan pattern.

Principle of working of SEM.

- Incoming (primary) e^- can either be "reflected" (backscattered) from a bulk specimen or can release secondary electrons.

- Primary electrons are focused onto a small-dimel diameter electron probe that is scanned across the specimen

- Electrostatic and magnetic feilds, applied at right angles to the beam, can be used to change its directⁿ of travel.
- By scanning simultaneously in two perpendicular directions, a square or rectangular area of specimen (known as a rastered) can be covered.
- Image of this area can be formed by collecting secondary e⁻ from each point on specimen.
- Corresponding images are also formed by the detecors (additional) which collect x rays and back scattered electrons.

* Preparation of nanomaterials :-

(Making of sandwich layer)

* Doctor's blade technique :-

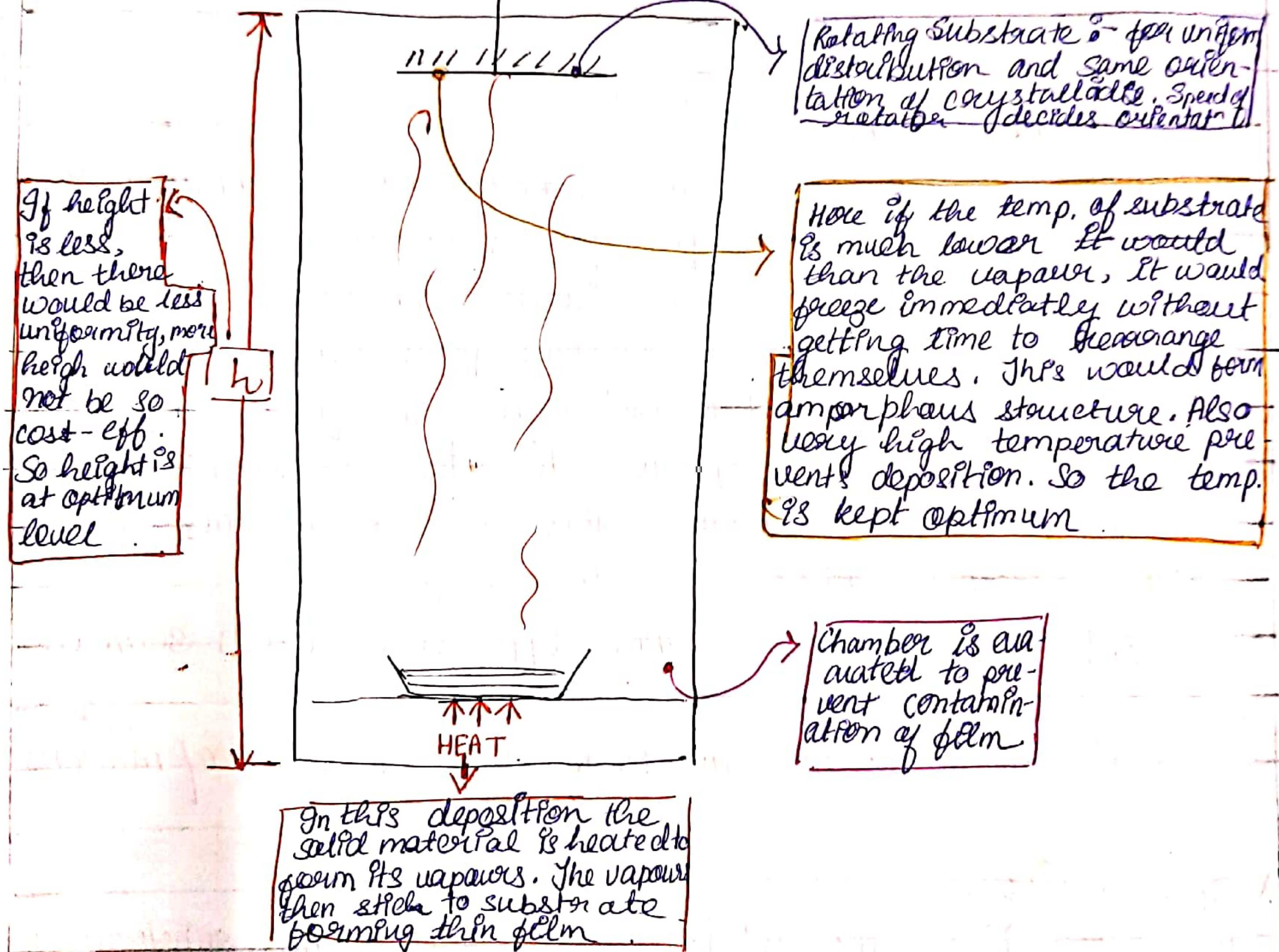
This method is also aptly named as knife coating or knife-over-edge coating, due to transfer of reel to reel coating. The stages of this technique are ~~suma~~ summarised as. movement of a substrate at a constant speed under a blade, with specific height and contact angle. The function of this blade is to spread the paste onto the surface homogeneously and get a fixed film. This method can also be performed by running blade over the surface.

Disadvantage :- Not precise. Also difficult to reach same levels of uniformity.
- Cannot create films with thickness less than 10s of microns.

* Spin Coating :-
- In spin coating, the solⁿ is dispensed onto a flat substrate which is either already rotating or subsequently begins to rotate.
- The centripetal force shears the solⁿ, causing it to be distributed evenly across surface as thin film.
  ↳ This method leads to creatⁿ of voids in b/w which is advantageous for making sensors.

* Spray meter method
Soln sprayed over the substrate.
↑ Smoke sensors are made using one of the above methods.
But for LED we use,

* Physical Vapour deposition :- (PVD)
PVD coating refers to a variety of thin film deposition techniques where solid material is vaporised in vaccum environment and deposited on substrates as a pure material or alloy composition coating.
⇒ Thermal vapour deposition.



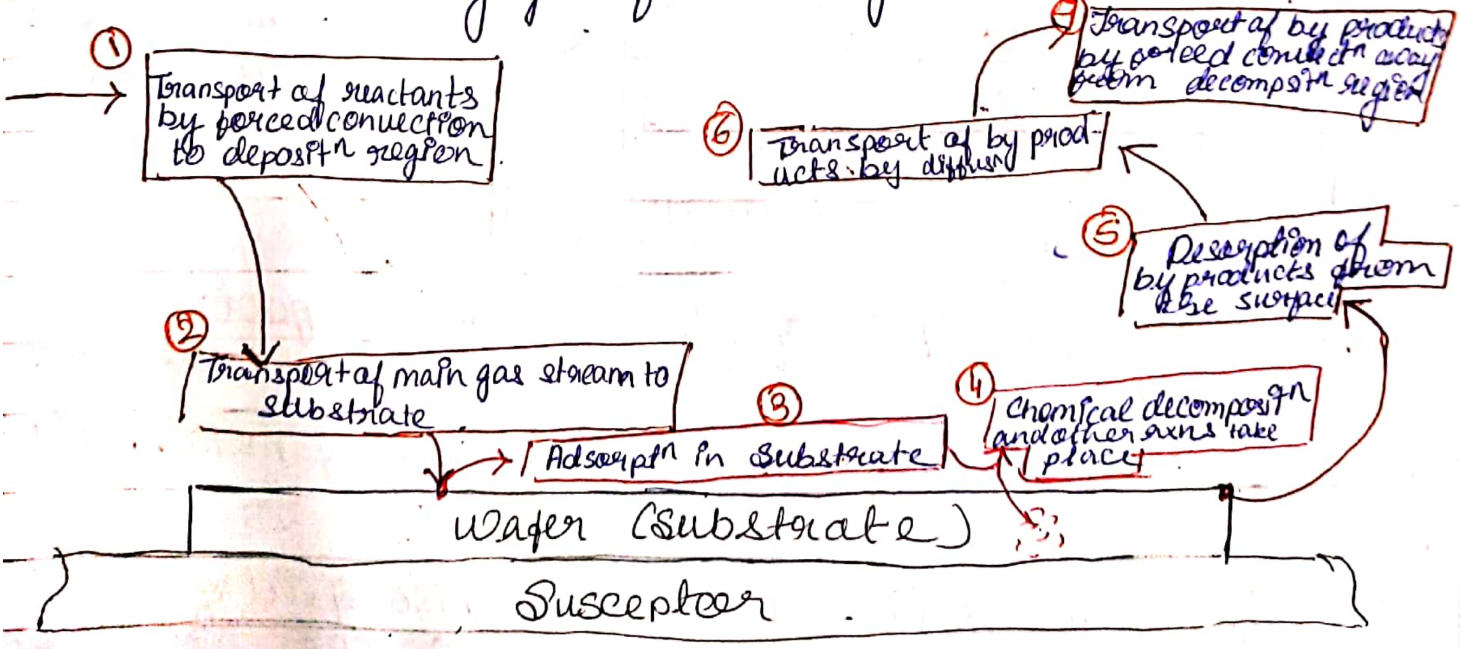
* Electron bean evaporation :- e⁻ beam ea evaporation is a form of PVD in which target material to be used as coating is bombarded with an e⁻ beam from a charged tungsten filament to evaporate and convert it to a gaseous state for depositn on substrate.

* Sputtering

- Sputtering involves bombardment of target material with high energy particles that are to be deposited on a substrate.
- The substrates to be coated are placed in a vaccum chamber containing inert gas (generally Ar) and (-)ve electric charge is placed on a target material to be deposited, causing plasma in the chamber to glow. Atoms are "sputtered off" the target by collision with Ar gas atoms, carrying these across vaccum chamber and are deposited as thin films.

* Chemical vapour deposition :- (CVD)

- Chemical vapour deposition is a chemical process used to produce high purity, high performance in solid materials.
- In CVD process, the substrate is exposed to one or more precursors* which react and decompose on the substate surface to produce desired deposit.
- During this process, volatile by products are also produced, which are removed by gas flow through the rxn chamber.

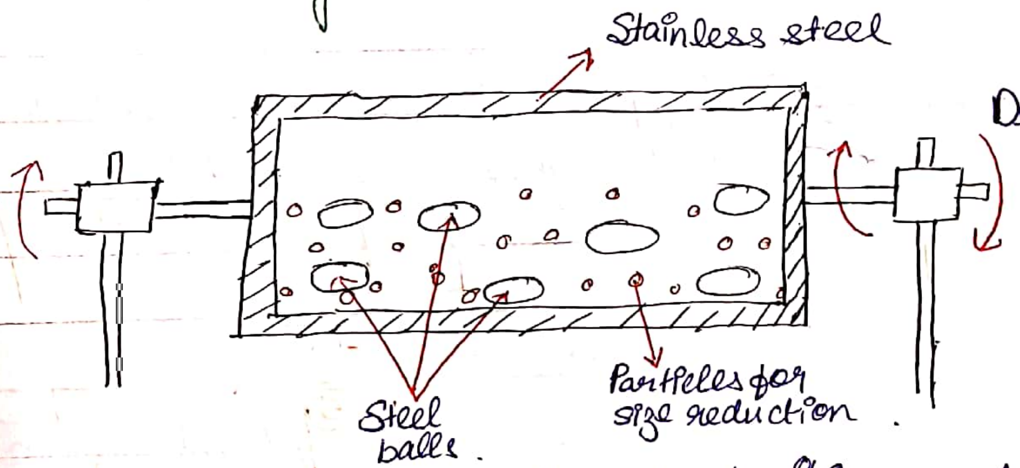


Seven Steps of CVD.

* Difference between PVD and CVD.

	PVD	CVD.
Defination	PVD is 'physical' vapour deposition	CVD is 'Chemical' vapour depositⁿ.
Coating material	Solid form	gaseous form.
Method.	Atoms are moving and depositing on the surface	The gaseous molecules will react with the Substrate
Deposition Temperature	Deposits at relatively low temperature (250°c - 450°c)	Deposits at relatively high temperature (450°c to 1050°c)
Applications	Suitable for coating tools that are used in applications that demand a tough cutting edge.	Mainly used for depositing compound protective coatings.

* Ball milling



→ Also known as pebbel mill and tumbling mill.

→ Works on the principle of attrition (Rubbing) and impact Fraction (size reductⁿ)

→ Here 30-50% of space is occupied by diff. sizes of metal balls and 60% (approx.) by material.

→ Here the drum continuously rotates. Also speed of rotation is very important. If the rotation speed is high, the material and ball would stick to walls of the drume due to

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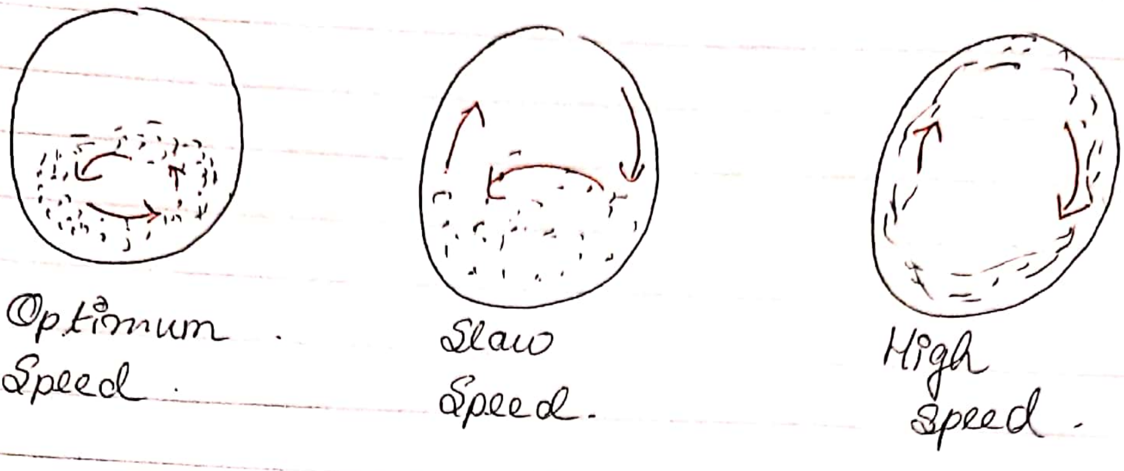
high centripetal force. While due to slow speed, balls would roll over each other. So the speed is kept optimum for size reduction.



*Uses

- Small + avg size mills are used for grinding of drugs / for grinding suspensions.
- Max^{m} capacity of ball mills are used for manufacturing of pharmaceutical chemicals.
- Grinds materials such as coals, pigments etc.

* Advantages.

→ Produces fine powder (particle size : 5-10 micron)
→ Suitable for milling toxic materials
→ Has wide ~~used~~ use in pharma industry.
→ Can be used for continuous operations.
→ Used for milling abbressive materials.

* Disadvantages.

→ Contamination of product may happen as a result of wear and tear occurring from balls and walls.
→ High machine noise level, specially hollow cylinder is made up of metal but less noise when rubber is used.
→ Milling takes a long time and is difficult to clean after use.

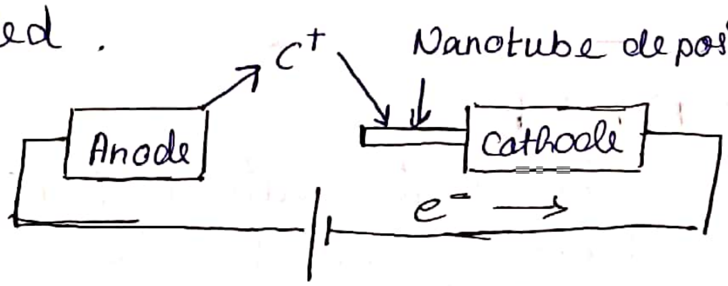
* Carbon nanotubes

Carbon nanotubes are hollow cylinderical tubes. The length of carbon nanotubes may vary from 1 to 20 nm. The ends are closed with caps containing pentagonal rings. There are two types of carbon nanotubes single walled and multiwalled. The single walle carbon nanotubes are of 3 types (i) arm-chair (ii) zig-zag and (iii) chiral type structure.

Formation :-

There are a no. of methods for making carbon nanotubes.

i). Plasma arcing method : Carbon nanotubes are prepared by putting electric current across two carbonaceous electrodes [graphite] as in a helium or argon ~~ato~~ atmosphere. This method is called plasma arcing method. In this method, evaporation of one electrode [anode] takes place as cations, and the particles are deposited at other electrode. The depositⁿ on the cathode are nanotubes. Normally multi-walled nanotubes are formed from plasma arcing. Single walled nanotubes are formed if electrodes are bored out and Co or other metals are included.



ii). Laser method :- Large quantities of single walled nanotubes can ~~pe~~ be prepared by dual-pulsed laser vaporisation method. In this method, samples can be prepared laser vaporisation of graphite rods with equal amounts of Cobalt and Nickel at 1200°C in flowing Ar. After this, heat treatment is carried out at 1000°C in vaccum to remove C_{60} and other fullerenes. The first lazer vaporisatⁿ follow pulse is followed by second for more uniform vaporisation. The product appears as a mat of ropes having a diameter of 10 - 20 nm and leg length of 100 μm or more. The diameter of the tubes can be controlled by varying the parameters such as growing temperature and catalyst composition. The other methods include arcing in presence of cobalt, ball milling, CVD, solar energy pyrolysis @ low temp., heat treatment of polymers etc.

Properties of nanotubes

→ They are mechanically robust.
→ They are 6 times lighter, 10 times stiffer and 20 times stronger than ~~stel~~ steel.
→ The tube behaves as a metal and as a semiconductor. As a metal, its electrical conductivity is 1000 times more than that of a copper.
→ Its electrical conductivity is function of its diameter, conductivity in multiwalled nanotubes is quite complex.

Applications of Nanotubes

i). Electronics : The single walled nanotube can act as a transistor. Pairs of nanatubes or crossed show as logic structures. A single nanatube with a natural junctⁿ acts as a rectifying diode. Transistor nanotube circuits are built by drawing a single nanotube over 3 parallel gold electrodes, adding a poly-

-mer b/w electrodes and sprinkling potassium atoms on top.

ii). Hydrogen storage :- Nanotubes can act as axles in nanomachines, Building gearteeth on nanotube is favoured to translate different rotatne motions

iii). Mechanical machines :- Nanotubes can store hydrogen and also helium, oxides and metals like copper.

iv). Space elevators :- Long filaments of nanotubes are used in fibre - reinforced plastics, these have less weight and are thus used in airplanes, space ships and vehicles. They are also used in thermal protection of spacecraft during re-entry into the atmosphere.

v). Hospitals :- They are thin and thus can penetrate skin w/o pain. Blood can be drawn from diabetic patients through nanostraws to know glucose levels and to inject insulin whenever required.

* Applications of nanotechnology

i). In microelectronics :- In microelectronics, reductn of size of electric components leads to faster switching times. It includes fabricatn of nanowires used in semiconductors

ii). Machine tools :- Some nano crystalline material such as tungsten carbide, tantalum carbide and titanium carbide are harder than conventional materials; so they are used in cutting tools and drill bits. Nanocrystalline silicon nitride and silicon carbide are used in manufacturing of high strength springs, ball bearings and value lifters.

iii). High power magnets :- Magnetic strength of material is directly proportional to the surface area per unit vol^m. The magnetic nanocrystalline yttrium - samarium - cabalt possess very high magnetic properties. Their applicat^ns are in submarines, MRI and ultrasensitive analytical instruments.

iv). In television or in monitor :- In screens, the resolution depends upon the pixel size and increases with decrease in pixel size. Materials like nanocrystalline selenide, zinc sulphide, lead telluride and cadmium sulphide synthesised by sol-gel method improve resolution.

v). Aerogels :- Aerogel are nanocrystalline materials. They are porous and hence air is trapped at the interstices. Using these materials for insulation at offices and homes leads to drastic reduction in cooling and heating bills by saving power. These materials are also used as materials for smart windows, so that the materials becomed darkened when sun is too bright and lightened when sun is not shining bright

vi). Energy effeciency :- For illumination, energy consumpt^n can be greatly reduced using quantum caged atoms or light emitting diodes (LEDs) instead of ordinary filament bulbs. Nanostructures with a continum of energy band gaps have an increased solar energy conversion effeciency as compared to ordinary semiconductor solar cells.

vii). Textiles :- Clothes made of nanofibres are water and stain repellent and wrinkle free. They can be washed less frequently