UNIT III: MATERIAL CHEMISTRY

Part I : *Non-elemental semiconducting materials*:- Stoichiometric, controlled valency & chalcogen photo/semiconductors-preparation of semiconductors (distillation, zone refining, Czochralski crystal pulling, epitaxy, diffusion, ion implantation) - Semiconductor devices (p-n junction diode as rectifier, junction transistor).
Insulators & magnetic materials: electrical insulators-ferro and ferri magnetism-Hall effect and its applications.

Part II:
Nano materials:- Introduction-sol-gel method- characterization by BET, SEM and TEM methods- applications of graphene-carbon nanotubes and fullerenes: Types, preparation and applications
Liquid crystals:- Introduction-types-applications.

Super conductors:-Type –I, Type II-characteristics and applications

* NON- ELEMENTAL SEMICONDUCTORS:-

These semiconductors are formed by the combination of elements of group III-V or group II-VI and certain other compounds which have valencies in non-stiochimetric compositions

→ stiochimetric semi-conductors:-

The crystal and band structure similar to that of Si & Ge. are developed by the combination of group III and group V elements and group II & group VI elements named as. stiochemetric semiconductors. for example Ga-As semiconductor. The $4s^2$, $4p^1$ level of Ga and $4s^2$, $4p^3$ level of to Overlap to give rise to hybrid band containing 4N electrons per N atom of Ga and As with ferry energy gap 2.24(eV) The following is the list of some stiochemetric semiconductors and their fermi energy gaps

Group III & V combination

Semiconductor	Fermi energy gap
GaP	2.24
GaAs	1.35
Gasb	0.67
In As	0.36

Group II & VI combination

Semiconductor	Fermi energy gap
cds	2.42
Cdse	1.74
Pbs	0.37

characterstics:-

1. They have wide energy gap, which leads to broad exhaustion zone with high conductivities, Hence they can be used at wider range of temperatures.
2. It is possible to alter the energy gap (E_F) of these semiconductors by substituting elements in its composition by an element of lower atomic number belonging to the same group for ex:- In GaP, If p is replaced by As the energy gap reduces from 2.24 to 1.35 (eV)
3. They can be doped to n or p-type semiconductors

→ Controlled valency semiconductors:-

$Ni^{2+}_{0.7} Ni^{3+}_{0.2} O$ is a hopping semiconductor producing hopping semiconductivity by hopping of electrons from Ni^{2+} to Ni^{3+} ions the concentration and conductivity of Ni^{3+} is controlled by the addition of small amount of Li^{+} ions.

$$LiO + NiO + O_2 \longrightarrow Li_x Ni^{2+}_{-2x} Ni^{3+}_x O$$

The semiconductors show conductivities depending on temparatures and find applications as thermistors These semiconductors can be used over a wide range of tempurature at 200°C the compound containing the compo-

...on $Li_{0.05}\, Ni^{2+}_{0.9}\, Ni^{3+}_{0.05}\, O$ is electroneutral semiconductor which is shown as below

Positive charge	Negitive charge
$Li^{+}_{0.05} = 0.05 \times 1 = 0.05$	$O^{2} = 2$
$Ni^{2+}_{0.9} = 0.9 \times 2 = 1.8$	
$Ni^{3+}_{0.05} = 0.05 \times 3 = 0.15$	
2.0	2

Thus $Li^{+}_{0.05}, Ni^{2+}_{0.9}, Ni^{3+}_{0.05}\, O$ is neutral semiconductor.

Chalcogen photo semiconductors:-

Oxygen (O), sulphur (S), selenium (Se) and Tellurium (Te) are collectively called chalcogens or ore forming elements because a large no. of metal ores are oxides (or) sulphides

Characterstics:-

1. They behave as semiconductors or photoconductors either alone or by combining with other elements
2. They rapidly form glass on cooling and viscous liquid on melting.
3. Chalcogen based glasses have conductivities in the range of $10^{-3} - 10^{-13}$ mho/cm
4. The conductivities of pure chalcogens increase with increase in atomic mass.
5. Selenium is an excellent photo conductor. Its conductivity increases enormously on exposing to light. Hence it is used in photo copying process (xerox)

* Preparation of semiconductors:-

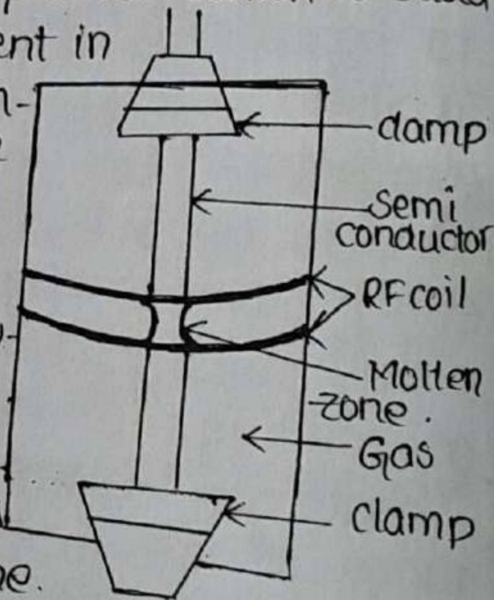
The semiconducting elements used for the application of semiconductor devices must be 99.99% pure i.e., one atom of impurity for every 10^{6} atoms of Si or Ge. To prepare such ultra pure materials the following steps were involved

Preparation of ultra pure Ge:-

($GeCl_4$) Germanium tetrachloride is used as a starting material, which contains arsenic (As) impurity which is removed as $AsCl_3$ and seperated by distillation

a) Distillation:- It is a process where seperation is carried out by taking the difference in boiling points as advantage Ge is taken in a series of stills with a layer of HCl over it and Heated it, while passing chlorine through it. the vapour produced were collected and passed into a fractionality column. the distilled vapours are collected into a recieved placed in ice bath. pure $GeCl_4$ thus obtained is treated with water to get GeO which is reduced in as atmosphere of N_2 to elemental germanium, which is further subject purifaction by zone refining.

b) Zone-refining:- It is Metallurgical process which is based on principle that the impurities present in a Metal are more soluble in molten metal than in solid metal. For the purification of Ge Vertical zone refiner is used. A rod of Ge to be purified is clamped and heated by RF coil is moved down, the impurities move with the molten part of the Material. pure Ge rod solidies at the upper portion. the process is repeated several times to reduce the impurity level & lower end of rod is removed after getting the desired purity because it is concentrated with impurities. By zone refining process the impurity level 1 atom in 10^{12} atoms of Ge is obtained



c) preparation of ultra pure silicon:- It is prepared by following Method

Chemical Method:- Trichlorosaline is first distilled to get pure trichlorosaline than it is reduced to elemental silicon by heating in an atmosphere of hydrogen by bubbling hydrogen through trichlorosaline which vapourizes

The vapours are fed into a tubular furnace fitted with a highly pure silicon rod and heated to 950°c. At this temperature, the vapours of trichlorosilane decompose leav-ing behind pure silicon on the surface of the highly pure silicon rod. the thickness of silicon rod increases from 2.5 to 10cm.

Hcl vapour produced in the reaction are removed throu-gh a vent. It cannot be adopted for the preparation of ultrapure silicon, because boron impurity has same solubility in molten and solid silicon and a high temperature is required to melt silicon.

→ Preparation of single crystals of si or Ge:-

The base requirement for the fabrication of a semi-conductor used must be a single crystal. The preparation of Si and Ge produces polycrystalline products i.e., crystals of various size. Hence single crystal of Si and Ge are produced by Czohralski crystal pulling technique.

Czochralski crystal pulling technique:- This process was named after the polist scientist Jan Czochralski who invented the Method in 1916 by accident while studying crystallization Method.

In this Method single crystals are grown in such a way that during crystal growth atoms reproduce the same atomic arrangement as that of the seed crystal. The process begins when the chamber which contains a crucible with silicon is heated to approximately 1500°c. when silicon is fully Melt, a small sp seed crystal Mounted on the end of rotating shaft is slowly Lowered until it just dips below the surface of Molten silicon. The shaft rotates in anticlockwise & the crucible in clockwise direction The rotating rod is then drawn upwards very slowly about 25mm per hour when making a crystal of silicon allowing in the form of boule to be formed. The boule can be form one to two meters, depending on the amount of silicon in the crucible

a) Melting of poly silicon b) Introduction of seed crystal c) Begining the crystal growth d) crystal pulling e) formed crystal with a residence of silicon

when silicon is grown in silica crucible O_2 from crucible is introduced as an impurity at a concentration of 10^{18} cm^3. Careful an annealing process condition were adopted to remove. Oxygen. The above process is adopted even for the crystal pulling of germanium

→ **Doping:-** Introducing an impurity into the semiconducting crystal is called doping. Doping is carried out by an expitaxy diffusion implantation techniques. Doping is carried out in the crystal pulling state. calculated amount of dopants are added to the Melt before crystal pulling.

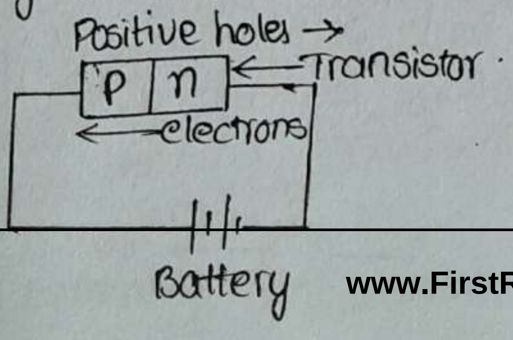
a) **Epitaxy:-** It is a process of deposition of a crystalline over layer on a crystalline subtrate The overlayer can be called as an expitaxial film. the term epitaxy comes from Greek - epi means 'over' and taxy Means "ordered Manner" Epitaxy refers to deposition of crystalline over layer on a crystalline substrate. which acts as seed crystal. The following are some of techniques molecular beam epitaxy. A source of Material is heated to produce an evoparated beam of particles. which ~~treate~~ travel through high vaccum to the substrate where they condense MBE has lower throughout than other forms of epitaxy. This is widely used for growing group III, IV & V semiconductor crystals

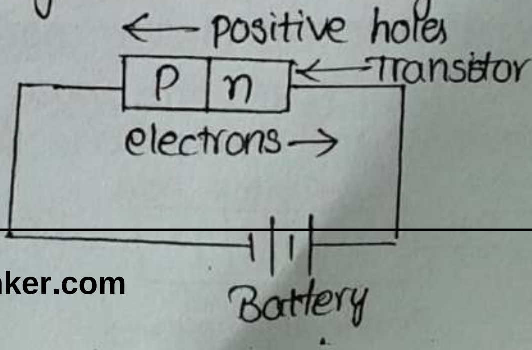
b) **Diffusion:-** An epitaxial layer can be doped during deposition by adding impurities to source gas such as Arsine, phosphine. The concentration of impurity in the gas phase determines the concentration in deposited film. the impurities change the deposition rate ~~At~~ high temparature the chemical vapour deposition May allow dopants to diffuse into the growing layer from layer to other in water p-type Ge water is heated just below the Melting point in an atmosphere of n-type dopant such as P or Sb causing diffusion of impurity into the material and produces pn-type Semiconducting Material.

c) Ion implantation technique:- In this a semi-conductor Material is bombarded with an electrically controlled beam having higher energy of 10 kev containing impurity ions like boron or phosphorous. this results in the implantation of some dopants into semiconducting crystals Ion implantation method is extensively used in the fabrication of high frequency devices.

* P-n JUNCTION AS A RECTIFIER :-

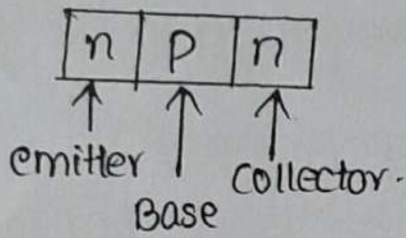
Current from an outside source is allowed to flow through a rectifier only in one direction. and this is very useful because it helps in converting alternate current to direct current. The function of p-n junction as rectifier is discussed below. A transistor with two zones, one p-type and other n-type with p,n-junction in between is known diode If p-type semiconductor region is connected to the positive terminal of battery and n-type region is connected to the negative terminal of the same battery. From n-type region electrons with migrate towards p,n-junction. where as holes will migrate towards the p-n junction At the p-n junction of diode, The Migration electrons from the n-type region move into the vacant holes in valancy band of p-type region. This Migration of electrons and holes can continue and current flows as long as the external voltage than a battery is supplied.

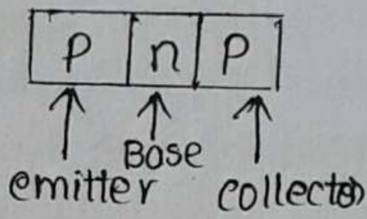




when the connection is reversed i.e., p-type region is connecting to the negetive terminal of the battery & n-type region is connecting to the positive terminal of battery the positive holes move away from p-n junction in p-type region and the electrons migrate away from p-n junction in the n-type region The current doesn't flow at junction as there are no electrons or positive Holes

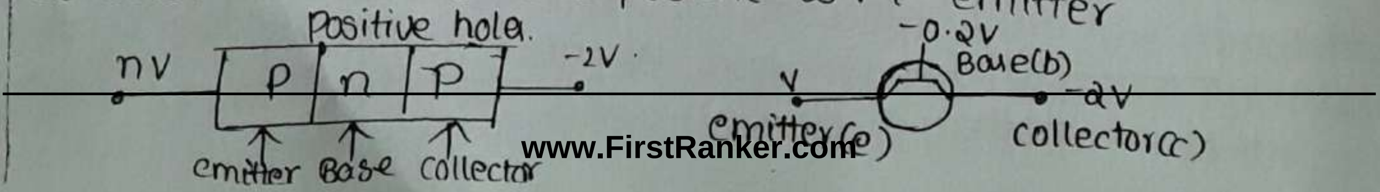
* JUNCTION TRANSISTORS:- They are single crystals of silicon which have been doped to give three zones, either p-n-p or n-p-n as shown below.





Different voltages must be applied to the three regions of transistor to make it work w.r.t emitter the base is typically -0.2V & the collector is typically -2volts.

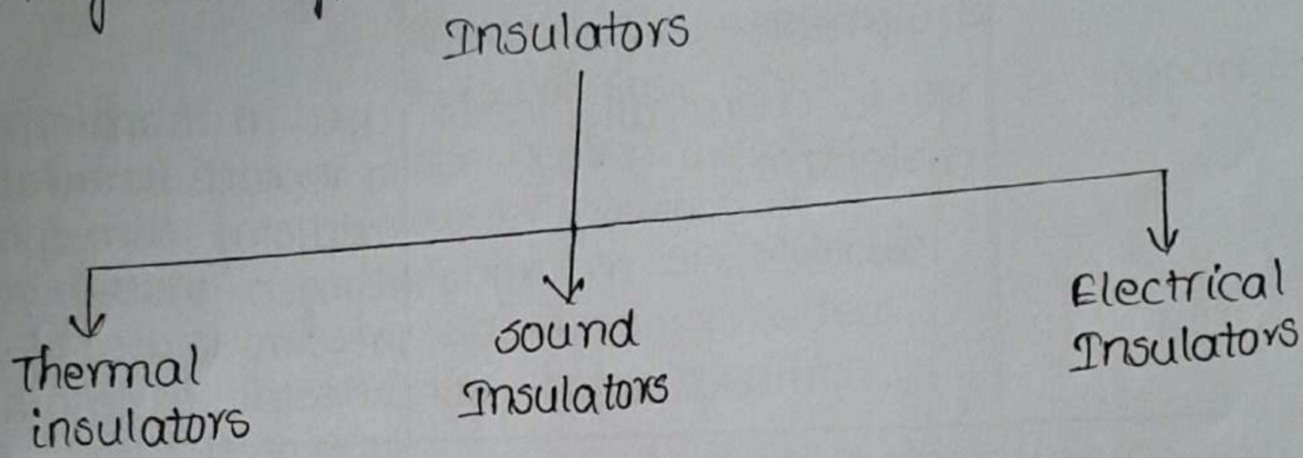
In p-n-p the charge carriers in the emitter are +ve holes, which migrate from emitter at 0 V to base -0.2V. The +ve holes cross the emitter/base p-n junction In n-type base region some holes combine with electrons & are destroyed electrons flow in the reverse direction from base to emitter. There is thus a small base current. Since the collector has much greater Negative voltage & base is very thin, Most of positive holes pass through the base to collector, where they combine with electrons from positive holes Typically if the emitter current is 1mA, The base current is 0.02mA and the collector current is 0.98mA The n-p-n transistor work in a similar way, except the polarity of the base voltage is reversed. Thus the collector and base are positive w.r.t emitter



Application of Transistor:- They are Most widely as i) amplifiers and oscillators in radio, T.V, computers & hi-fi circuits, phototransistors, solar cells, detectors for ionizing radiations, thermisters and tunnel diodes

* Insulators:- The substance which are capable of retarding (or) prohibiting the flow of heat or electricity (or) sound through them are known as Insulators

They are 3 types:-



→ Classification of Insulators:-

According to American institute of electrical engineers all insulating materials are divided into three classes according to their constitution They are.

a) Gaseous Insulators
b) Liquid Insulating Materials &
c) Solid Insulators.

→ a) Gaseous :-

Dielectric gases are used on both as insulants and heat transfer medium. The major problem associated with them are abnormalities in dielectric behaviour at high pressures, temparature instability and fire hazards. Taking into consideration the dielectric strength, dielectric loss, chemical stability, corrosion resistance etc.. They May be classified as follows

Insulator	Properties	Applications
1. Simple gases i) Air	Most important of all dielectric gases. It acts as a relible insulating material when voltages are not very high. However Oxygen in air causes Oxidation, which reduces the life of an electrical equipment	It provides insulation between overhead transmission lines without any cost.
b) Nitrogen	It is chemically inert dielectric.	used in transformers to replace harmful. Oxidising atmosphere Nitrogen under high pressure is used as dielectric in certain types of electrical capacitors
c) hydrogen	It is of special interest due to its lightness & coolant property. Organic insulators in contact with hydrogen are less susceptible to ageing because there is no oxidising effect.	used as coolant in electrical Machines like large turbo generators, synochronous condensers etc..
d) Carbondioxide	The dielectric strength of CO_2 is comparable with that of air.	CO_2 is used as an insulant in certain types of fixed capacitors and is also used as preimpregnant for oil filled high voltage. apparatus such as cables and transformers.

2. Electronegative gases like SF_6 & CCl_4	They have high dielectric strength as compared to N_2 & air for eg: The dielectric strength of SF_6 is 235 times & of carbon tetra chloride is 6.33 times that of the air. These gases are also non-inflammable & non-explosive. SF_6 is not toxic, stable when heated upto 800°c. However presence of sulphur in SF_6 molecule yield corrosion effect under some condition.	SF_6 is used in electrical devices like capacitors, Cables etc.

2. **Liquid Insulating Material:-** Insulating liquids are used for purely dielectric purposes in order to eliminate air or other gases, or as an insulating & Heat transfer medium. usually liquid insulants are used in conjunction with solid Insulants. These can be broadly classified into

Insulator	Properties.	Application.
1. Mineral Oils	These are obtained from Crude petroleum. these electrical Properties & resistance to thermal oxidation are greatly influenced by presence of non hydro carbon compound O_2, Sulphur, N_2 etc. These are used in the temperature range of -50°c to 110°c.	They find extensive application as insulating oils in cables, capacitors transformers switch gears etc..
ii) Askarels	These are synthetic insulating Liquids which are non inflammable and which under the influence of electric	Askarels are used as transformer fluids. In practice, the askarels are

	arc does not decompose to produce inflammable gases. These are also used in the temparature range of -50°c to 110°c. Most widely used askarels are chlorinated hydrocarbons i.e chlorinated diphenyl, penta chloride diphenyl, trichloro diphenyl, hexa chloro diphenyl, trichloro ben zene. Further askarels possess excellent fire resistance, high dielectric strength, dielectric constant of the order of 4to6 tolerable dielectric loss at normal temparature & power-fre -quencies, adequate thermal; chemical and electrical stability.	usually used to impregnate cellu -losic insulating material such as paper or press board etc.
(iii) Silicone fluids	These are used in the temparature range of -90°c to 220°c. Silicone fluids are organic compounds of silicone with a structure of alternate atoms of silicone and oxygen. They are clear water like white liquids with an only consistency and are available with a wide range of viscosity. They have stability at high temparatures, non-corrosive to metals upto 200°c. Silicone fluids have a tendency to breakdown in the presence of electric arc to give consideration (or) considerable amount of gases and residue consisting of c, sic & SiO_2.	they are used as coolants for radar. Pulse, aircrafts & radio transformers. However they are too costly to be used as coolants for large power transformers. They are also not reco-mmonded as switch gear oils
iv) Flourinated fluids:	These are used in the temperature range of -50°c of 200°c. They have a very high chemical stability	They are used in small size electric & radio devices electronic

compounds	[illegible]se the flourine non-inflammable and their substituted organic vapours are non-explosive. They ensure much better heat transfer from the windings & Magnetic circuit than mineral oils or silicone fluids. However flourinated liquids are degraded in their electrical properties under the influence of moisture. Moreover they possess high voltality	transformers etc.
v) Synthetic Hydrocarbon Liquids:- eg:- polybutene & polypropylene	used in temparature range of -50° to 110°c. They have similar ~~dielectric, stability and oxidation thermo~~ dielectric strength thermal stability and oxidation suspectibilty as that of Mineral oils	They are used in high pressure gas-filled power cables & DC voltage capacitors, Viscous synthetic Hydrocarbon Liquids are also used as thickners of Mineral oils used for the impregnation of solid power cables.
vi) Organic ester Liquids:-	These operate in temperature range of -50° to 110°c. They possess Low dielectric Losses and high dielectric constant	They are well suited for certain high frequency capacitor applications
vii) Vegetable oils:- These include drying oils like linseed oil, non drying oils like castor, coconut, palm, olive, peanut oils	used in the temparature range -80° [illegible] to 100°c	Drying oils are used in formulation of Insulating varnishes, which are used in treatment of transformers and Motor coils etc. Non drying oils are used as plasticizers in insulating resin compositions which are applied as structural & insulating materials & coating composition in electrical equipments

c) Solid insulating Materials:- They are classified according to the temparature upto which they can be used, because insulating material retain their insulating property as long as certain temparature is not exceeded.

Insulator	Properties	Engg. Applications
i) paper & press boards are made from wood cellulose $(C_6H_{10}O_5)_n$ where n is very large number. paper is also made from rags, cotton linen and various types of humps	Paper and card boards made from alkaline wood cellulose Mechanically stronger and more heat resistant	paper and Press-boards are used for windings and cable coil insulation transformer insulation etc. Mineral oil impregnated Papers & boards are advantages in bushings and cables. while diphenyl & vegetable oil impregnated papers are Preferred for capacitors.
ii) Fibrous insulator like cotton, silk, wool, Jute, rayon, nylon, terylene, teflon, fibre-glass etc..	They have high mechanical strength, durability, cheapness, flexibility & easy processing. Their drawbacks include hygroscopicity and low dielectric strength.	They are used in conductor insulation, backing for mica insulation, manufactor of vanished cloth which finds wide application in electrical Machine & cables
Inorganic fibours Materials like asbestos, glass fibre possess greater heat resistance than organic fibrous Material	They operate at high temperatures (180°c) they possess elasticity, poor flexibility as compared to organic fibrous Materials	

iii) impregnating, coating, and bonding materials are synthetic high molecular weight organic & organo metallic compounds they are classified as.		
a) waxes, which are complex organic compound of Natural and synthetic origin.	They are soft and Mechanically weak.	Natural waxes have limited applications as insulants, but synthetic waxes are used as impregnants
b) insulating Varnishes are solutions of substance like bitumen, drying oil, resin etc.	coating varnishes from tough smooth, water proof films on the surface of objects. Hard solid films have low Hygroscopicity and they adhere well to surface	The Main application of insulating varnishes are impregnation coatings & adhesion impregnation for porous hard and fibrous insulant like paper, fibre yarn etc.
c) Bonding Material adhesives:- These are the solutions of Modified phenolic resins in alcohol	They are available in the form of films, tapes etc..	They are used in electric apparatus & low capacity electrical machines. They are used to seal separated insulated parts. Adhesive tapes are extensively used in stationary.
iv) Resins are Natural or artificially made organic substance of high m.wt		
a) Natural resin are copal, rosin shellac and amber.	shellac obtained from tropical trees possess high adhesive property	Rosin obtained from pine trees is used in the Manufacture of insulating varnishes

		Amber is used to make electrical insulating components in measuring instruments.
b) synthetic resins:- i) polythene is obtained by polymerization of ethylene.	It is available in pellet. powder, sheet, film rod, tube & foam forms	It is used as high frequency insulator in radio, television & communication circuit cables and also in power cables, Submarine cables etc...
ii) polystyrene is produced by polymerization of styrene. High polymeric. styrene. is hard rigid transparent solid.	It possess excellent dielectric properties. It is available in the form of transparent film rod, tube and foam forms.	It is used as dielectric in DC & high frequency capacitors, electrical bushings, telephones, flourescent ligh accessories etc.
iii) pvc is obtained by polymerisation of Vinyl chloride.	It is chemically inert mechanically strong, has extremely low Moisture absorption property, has high dielectric constant.	used in flexible wire. coverings, cable sheathings, insulating electric wires, and low voltage cables.
iv) teflon obtained by polymerization of tetraflouro ethylene.	It is available in rods, sheets, tapes, it is thermally & chemically Stable & can be used as insulant upto 327°C.	used as capacitor dielectric & insulating Material for almost all kinds of windings
v) epoxy resins:-	These resins posess excellent electrical & Mechanical properties.	Mostly used in Making insulators, bushings etc.. for. high voltages. Also used for. Making laminates & insulating Varnishes.
vi) polyester resins:-	They possess good. dielectric properties. and highly resistant to most acids, bases, Salts & solvents	Used in making paper, Cloth mat for electrical insulation. Its films are. used for wire and cable. insulations & in motors, transformers & capacitors

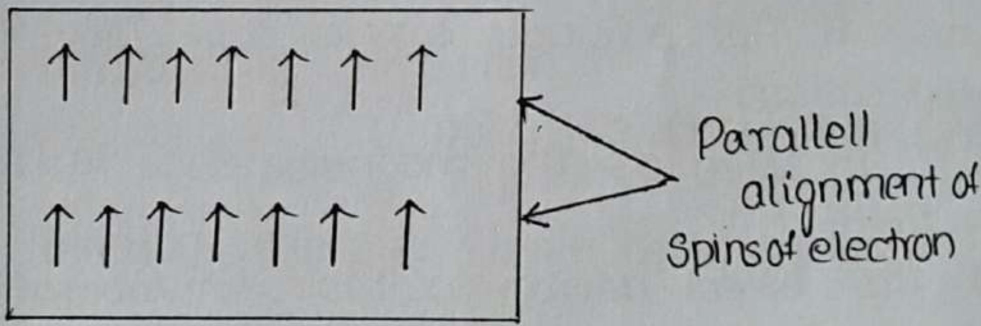
d. Rigid insulators

Glass:-	They possess low temperature coefficient, high dielectric constant & dielectric strength.	Used for wire covering line insulations, glass to metal seals & other electrical engineering applications

* Ferro Magnetism:- The atomic moments in these materials are very strong interactions, which are produced by electron exchange forces and results in parallell alignment of atomic moments. The electron exchange force is due to the relative operations of spins of two electrons.

The distinctive characterstics are spontaneous magnetization and magnet ordering temperature
Ex:- Fe, Ni and Co

* Ferri Magnetism:- As a result of crystalline structure of ionic compounds such as oxides, more complex Magnetic ordering occurs and one type. Magnetic Ordering is called ferri Magnetism.



* HALL EFFECT AND ITS APPLICATIONS:-

It is the production of a voltage difference across the electrical conductor, transverse to an electric current in the conductor and a magnetic field perpendicular to the current. It was discovered by Edwin Hall in 1879.

When a current carrying semiconductor is kept in a magnetic field. the charge carriers of the semiconductor experience a force in a direction perpendicular to both Magnetic field & current. At equilibrium a voltage.

appears at semiconductor edges. The simple formula for the Hall coefficient given above becomes more complex in semiconductors, where there carriers are generally both electrons & holes which may be present in different concentration & have different mobilities. For Moderate Magnetic fields the Hall coefficient is $R_H = \frac{p\mu_n^2 - n\mu_e^2}{e(p\mu_n + n\mu_e)^2}$.

or equivalently.

$$R_H = \frac{(p - nb^2)}{e(p+nb)^2}$$

with $b = \frac{\mu_e}{\mu_n}$.

where n is electron concentration, p = the hole concentration

μ_e = the electron mobility

μ_n = the hole mobility &

e = elementary change

For large applied fields the simple expression analogous to that for a single carrier type holds.

Applications:-

1. It is used as ~~mg~~ magnetometers to measure magnetic field
2. Hall effect devices suitable for laboratory instruments.
3. Hall effect sensors have mass application & analog-to-digital convertors
4. A hall effect thurster is used in space craft application
5. Industrially Hall effect joysticks are used to control. hydraulic valves, Scissor lifts, cranes, mining trucks etc..

* Nano materials :-

→ The materials like metals, Ceramics, polymeric materials (or) the Composite materials with dimensions and tolarences in the range of 1nm to 100 nm are called "nano materials."

→ One nanometre (nm) = One billianth (10^{-9}) of a meter

i.e., $1nm = (1/10^9)m$ (or) $10^{-9}m$

→ 1m = 39 inches = 3 feet

→ Centi = 10^{-2}

→ milli = 10^{-3}

→ micro = 10^{-6}

→ Nano = 10^{-9}

* Nanometer is used to measure the objects which are very small in size.

Ex:- Size of hydrogen atom = 0.1nm

→ water molecule < 1nm

→ RBC = 5000nm

→ Human hair = 50000 nm

→ Limit of human eye's visibitity = 10000nm

→ Diameter of a carbon nanotube = 1.3nm

* Due to their small size, Nanomaterials exhibit unique properties (different from those observed in bulk materials) like melting point, reactivity, reaction rates, electrical conductivity, colour, transparency etc.

* Nanomaterials may be biological, inorganic (or) Organic by their Origin

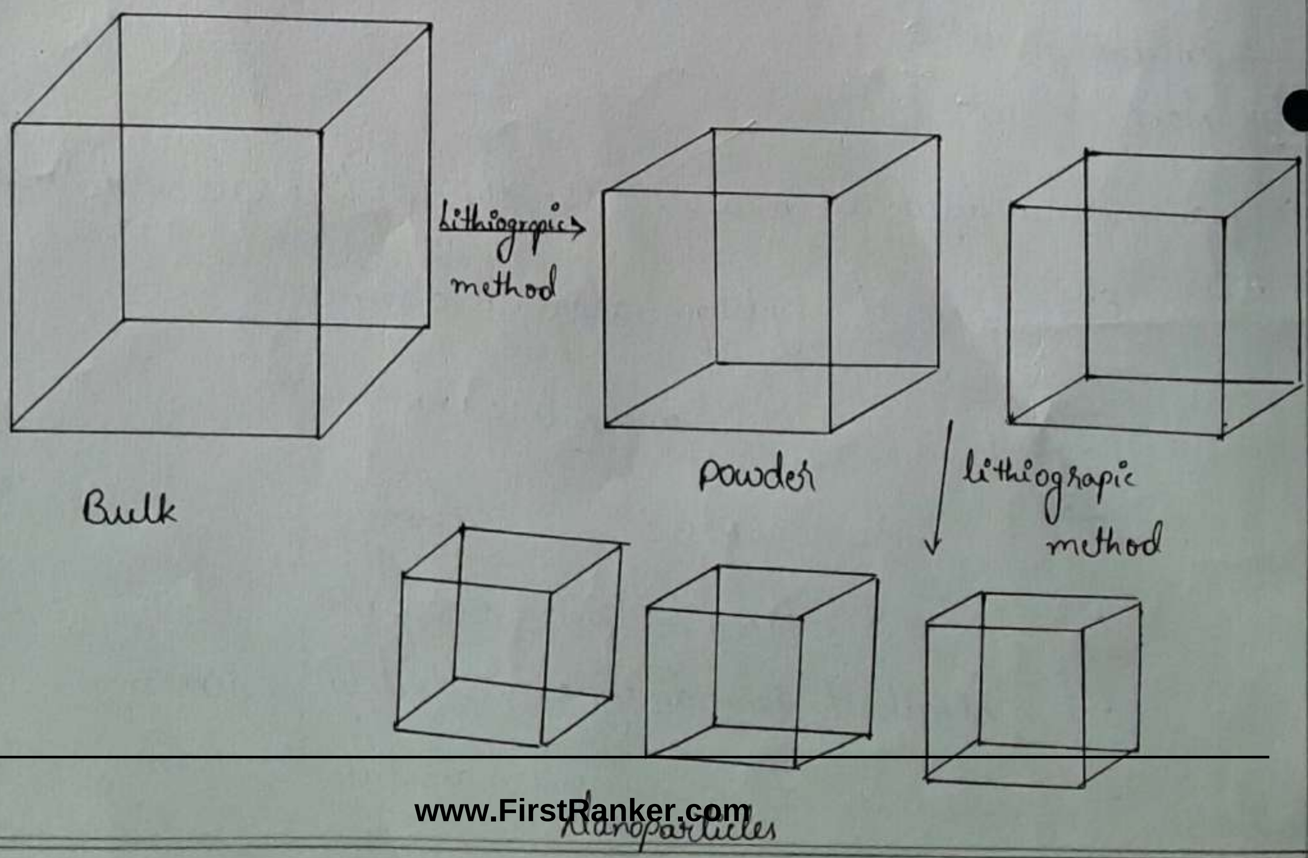
* A nanoparticle is defined as a small object that behaves as a whole unit in terms of its transport and properties and exhibits a number of special properties relative to bulk materials.

* **Methods of preparation of Nanomaterials :-**

1. **Top down approach :-**

→ In this method bulkmaterials are converted to powder and then to nanoparticles by making use of lithographic methods

→ This method is used in the microelectronic industry

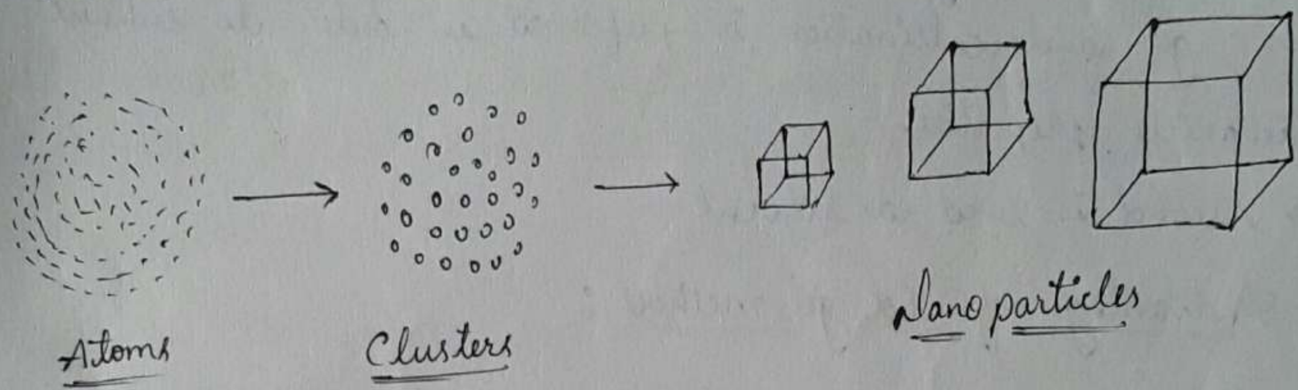


Bottom up approach :-

→ In this method very small particles like individual molecules (or) atoms are assembled to get clusters which in turn are aggrigated to get nanoparticles

→ This method is used to prepare a new class of nanomaterials.

Ex:- Fullerenes and polymer nano composites are prepared by this method.



* Sol-Gel method :-

→ Sol-gel method is bottom up approach for the synthesis of nano materials

→ A soil is a collidal (or) molecular suspension of solid particles of ions in a solvent

→ A gel is a semi rigid mass that forms when the solvent from sol begins to evaporate and particles (or) ions left behind begin to join together in a continuous net work.

→ sol-gel processing is wet chemical technic that uses a sol to produce an integrated network i.e., gel

→ Metal Oxides (or) metal chlorides undergo hydrolysis and polycondensation reactions to form a colloid ~~with~~ which is a system composed of nanoparticles dispersed in a solvent

→ The solvent evolves towards the formation of an inorganic continuous network containing a liquid phase (gel).

→ Formation of metle oxide involves conecting the (metles) metal centres with Oxo (M-O-M) (or) hydroxo (M-OH-M) bridges generating metal-oxo (or) metal-hydroxo polymers in the solution.

→ After a drying process the liquid phase is removed from the gel and calcination is performed in order to enhance the mechanicle properties.

→ Alcohol is used as solvent.

* Advantages of Sol-gel method:

→ Able to get uniform and small size powder

→ Can get new microstructure and composition at low temprature

→ Can produce uniform multicomponent systems

→ Better control over the reactions

* Chemicle reduction method:-

→ Chemical reduction method is also belongs to bottom up approach

→ Metal nano particles particularly silver nano particles are prepared by this method.

* Preparation of Silver Nano particles :-

→ For the preparation of silver nanoparticles silver nitrate solution (from 1 ppm to 6 ppm) and 8 % w/w sodium dodecyl sulphate (SDS) are used as metal salt ~~(procerss)~~ procurssor and metal stabilizing agent respectively.

→ Hydrazine hydrate (2-12 ppm) and citrate solution (1ppm) are used as reducing agents

→ The transparant colourless solution will be converted to pale yellow and red colour which indicates the formation of silver nano particles

→ To remove the excess silver ions the solution is washed with deionised water under nitrogen stream for three times

→ The nano particles are characterised by uv and x-ray crystallography

→ General preparation is carried out by mixing the metal ions salts with transfer agents and reducing agents

→ Different types of phase transfer agents are ~~(called)~~ used for the preparation of different metle nano particles.

→ Metal salt solution + metal salt ~~precursor~~ precursor + stabilizer + reducing agent ⟶ stand for sometime ⟶ Nanoparticles separate ⟶ purification ⟶ Centrifugation ⟶ Freeze drying ⟶ metal nano particles.

* Applications :-

→ Nano particles like silver, gold, platinum, etc are prepared by this method

* Brunaer - Emmett - Teller (Bet) method :-

→ Nano crystalline particles of $Co_xFe_{(3-x)}O_4$ are synthesized by combustion reaction method using iron nitrate, cobalt nitrate and urea with Asa's fuel without template and subsequent heat treatment

→ The process is simple and inexpensive since it does not involve intermediate decomposition (or) calcination steps

→ The maximum reaction temperature range 850 - 1010°c and combustion lasts for 30 seconds for all systems

→ The materials are washed with deionized water and the byproducts are rinsed off producing pure nano particles.

* Transmission electron microscopic (TEM) method :-

→ This is a method for synthesis of collidal platinum nano particles which is potentially important in the field of catalysis

→ Catalytic reactivity depends on size and shape of the particle.

→ A solution of potassium platinum chloride (0.00001M) is prepared in water and treated with 0.2 ml of 0.1 M sodium poly acrylate

→ The resulting solution is stirred with   for some 20 minutes

→ The platinum ions are reduced by bubbling H_2 gas for 5 mintes

→ The reaction vessel is sealed and overnight

→ The solution turns light golden and nanoparticles are purified and separated

* Properties of Nanomaterials :-

Nanoparticles are specific in their nature behaviour because the physical behaviour of the particles change with decreasing size of the particle

1. Properties based on size of particles :-

(a) Magnetic properties :-

Magnetic properties increase with decrease in the size of the material due to increased orderly electronic spins

(b) Melting point :-

Melting point of the nano materials increases, when compared with other materials depending on the size of the particles.

(c) Solubility :-

Solubility of nanomaterials is more than other material due to the decreased size.

(d) Colour :- The physical property colour is again size dependant. As the size of the particle decreases the colour of the material changes.

* Engineering applications of Nanomaterials :-

1. Electronics :-

(a) Commertial digital switching devices, integrated in 10^{12} devices on a single chip are fabricated

(b) High sensitivity and high selectivity environmentle sensors to sense gaseous chemicals like CO, NO, NO_2 and O_3 in high traffic environments are fabricated.

(c) In making light emitted electroluminiscence [illegible], which find application in flat panel display technologies like T.V, computer monitor, colour changing fabrics etc

2. Magnetic applications:-

Magnetic nanoparticles from iron and palladium have been found to self arrange automatically and these materials are extensively used in the manufacture of magnetic storage devices producing terabyte storage capabilities

3. Biomedical applications:-

(a) Drug delivary of bio medical drugs which are bounded to magnetic nano crystals to the region of body where the drug is required is carried out

ex:- Rare tumour causing cells can be targetted by nano crystals, the captured and removed from blood stream.

(b) Medical dignostics is a field which extensively use (~~nO~~) nanocrystals silica coated iron oxide nanocrystals with embedded magnetic colloidal particles are sent into blood stream where the antibody reacts and binds with the target harmone and move rapidly which can be separated and ~~Groove~~ ~~rapidly~~ detected from blood sample.

→ DNA detection through calorimetric technique by using oligonucleotide functionalised gold nanocrystals is developed.

Structural and mechanical material applications:-

(i) Coating nanocrystals of metals with ceramics is carried nanostructuring by getting the benefits of ceramics (corrosion resistant, hard and ware resistant) and metals (ambient ductility). These coatings are superior coatings.

(ii) Fabrication of ceramic components is easier through nano structuring.

→ By nanoscale distribution of tungsten carbide improves the life and performance of cutting tool material.

* Industrial catalysts should contain high surface area and capacity to make any material attach to their surface

→ Cerium Oxide, platinum, gold, molybdenum, nickel, nano particles are extensivly used as catalysts.

* Because of high tensile strength, light weight and flexible nature some nanomaterials like CNT are extensively used in aircraft industry

* Nanomaterials like fullerences are used extensively in making consumer goods, cleaning products and fabrics etc

* Agriculture is another field where nanomaterials find their use in delivary of genes and drugs to animals for health and genetic improvement and in delivary the biodegradable chemical for plant nourishment is adopted.

Fullerenes:-

→ Fullerene is defined as a molecule composed entirely of carbon, in the form of hollow sphere, ellipsoid (or) tube

→ Spherical fullerenes are also called ~~(bucky)~~ bucky balls as they resemble the balls used in football (Soccer) ~~as they resemble the balls used in~~

→ Fullerenes are similar in structure to graphite which is composed of graphene sheets of linked hexagonal rings, may also contain pentagonal (or) heptagonal

→ The first ~~(the)~~ fullerene molecule was prepared in 1985 Richard Smally and H. Kroto at Rice university, USA, called carbon-60 (C_{60}). They named that as "Buckminister fullerence" after the name of an architect Buckminister fuller, well known for building geodesic domes.

→ They were awarded Noble prize in 1996 ~~(in)~~ for their work

* Types of fullerenes :-

Due to structural variations fullerenes exist in the following different types

(a) Buckyball clusters
(b) Carbon nano tubes
(c) Mega tubes
(d) polymers
(e) Nano 'onions'
(f) linked ball and chain dimers

Buckminster Fullerene:

→ In 1985, it was discovered by R. Smalley and H. kroto at Rice university, USA.

→ They named it as Buckminster fullerene after the name of an architect Buckminstr fullerene, who is well known for building geodesic domes.

→ It is the smallest fullerence molecule containing pentagonal and hexagonal Rings

→ It is naturally Occuring fullerene found in soot.

→ The structure C_{60} is called turncated icosahedron, which resembles foot ball containing 20 hexagons and 12 pentagons

→ The ~~wander~~ vanderwall's diameter of C_{60} is 1.1nm and its avrage bond length is 1.4 A°

→ The smallest fullerene is dodeca hedral (C_{20})

BUCKMINSTER FULLERENE (C_{60})

→ Now several number of fullerenes are present such as C_{70}, C_{76}, C_{84}, C_{240}, and C_{540}

* Fullerenes are a class of closed cage carbon molecule, C_n, characteristically containing 12 pentagons and a variable number of hexagons.

$$\text{Number of hexagons} = \frac{(\text{Carbon atoms}, n) - 20}{2}$$

* Preparation of Fullerenes :-

→ A common method used to produce fullerenes is to send a large current between two nearby graphite electrodes in an inert atmosphere.

→ The resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated.

→ The fullerenes are extracted from soot using multi step procedure.

* Properties of Fullerenes :-

→ Fullerenes are stable with sp^2 ~~(hybridisation)~~ hybridised carbon atoms.

→ The reactivity of fullerenes is increased by attaching active groups in their surfaces.

* Solubility :- Fullerens are sparingly soluble in many solvents. Common solvents are toulene, CS_2.

* Quantum mechanics:-

wave particle duality is exhibited by fullerenes as a result several sculptures symbolizing wave particle duality are created

* Hydrogenation:-

C_{60} exhibits a small degree of aromatic character, undergoes addition with hydrogen to polyhydro fullerenes.

* Halogenation:-

Addition of F, Cl and Br occur for C_{60} under various conditions, produce a vast number of halogenated derivatives.

Ex:- $C_{60}Br_8$ & $C_{60}Br_{24}$

* Addition of Oxygen:-

C_{60} can be oxygenated to epoxide $C_{60}O$ and Ozonisation of C_{60} in orthoxylene at 257 K gives Ozonide $C_{60}O_3$ which can be decomposed into 2 forms of $C_{60}O$ and the same decomposition (of) at 296k gives epoxide.

→ C_{60} is the most symmetric molecule.

→ physically, bucky balls are extreamely strong molecule, able to resist great preassure. They will bounce back to their original shape after being subjected to over 3000 atm.

* Applications of Fullerenes :-

→ Fullerenes can be added to polymer structure to create new copolymers with specific physical and mechanical properties

→ Fullerens have potential ability to transfer hydrogen. Therefore, they are used as catalysts for hydrogenation.

* In Medicine :-

Buckminster fullerene inhabit the HIV virus. C_{60} inhabits a key enzyme in human immunodeficiency virus known as HIV-1 protease which could inhabit the reproduction of HIV virus in (~~immune~~) immune cells when impregnated with He, C_{60} buckyballs can be used as chemical tracers in human body

* In solar Cells :-

The optical absorption properties of C_{60} match solar spectrum, hence finds its application in solar cells

* Carbon Nanotubes (CNT) :-

→ Carbon Nanotubes are (~~g~~) sheets of graphite about 0.4nm in diameter rolled up to make a tube of few nm in diametre.

→ Carbon nanotubes are called bucky tubes

→ CNT (~~discovered~~ in) was observed in 1991 in carbon rod of graphite electrodes during arc discharge.

→ First production of CNT was 1992 by arc discharge at the fundamentle research lab

* Preparation of CNT :-

1. Arc discharge method :-

→ By arc dischage of graphite electrode in presence of ionised gas to reach high tempratures and by using a current of 100 amps CNT was produced.

→ During this process, the carbon contained in the negative electrode sublimates because of high-discharge temprature.

→ This method has been widely used method of CNT synthesis.

→ The yeild is 30% and produces both single and multi-walled nanotube with lengths of upto 50 micrometers with few structural defects.

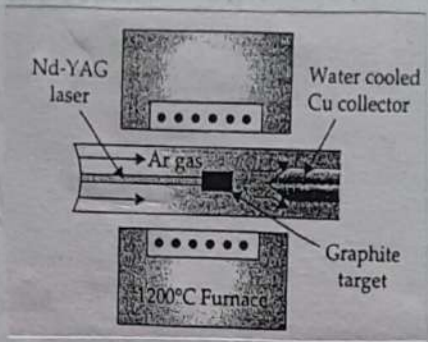
2. Chemical Vapour deposition (CVD) method :-

→ The method was developed in 2007 ~~in~~ at university of cincinnati, USA

→ ~~(Using)~~ During CVD process a substate was prepared with layer of metal catalyst nanoparticles (Ni (or) Co)

→ The substrate is heated to 700°c and a mixture of nitrogen and carbon containing acetylene (or) ethylene (or) ethanol (or) methane was passed

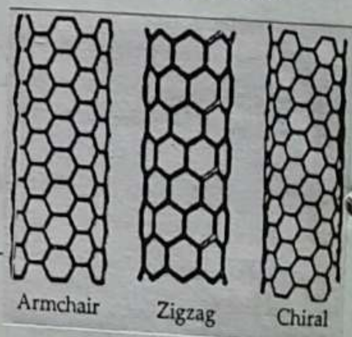
→ The CNT grows at the surface of the catalyst particle where the carbon containing gas is broken and carbon is transported to the edges of the particle where it forms CNT



→ CVD method is most promisable for industrial production of CNT because of its low cost and direct growth on the catalyst surface.

* Types of CNT :-

1) Single-walled carbon nanotubes (SWCNT) :-



→ These are different types depending on the manner in which the graphene sheets are rolled

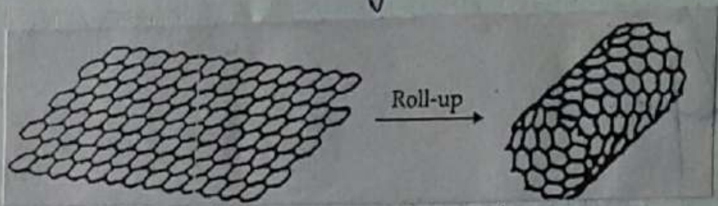
→ The basic varieties being zig-zag, arm chair and chiral.

→ Identification of a particular variety can be made by following pattern across the diameter of the tube and analyzing their cross sectional structure.

b) Multi-walled carbon nanotubes (MWCNT)

→ It consist of several concentric SWCNT with different diameters.

→ The forms are more complex here as each SWCNT can have different structures resulting in a variety of sequential arrangements



* Properties of CNT :-

1. Strength :- CNTS are strongest and stiffest materials due to covalent sp^2 bonds between the individual carbon atoms. CNT possess strength upto 100 gigapascals (GPa)

2. Hardness :-
Standard single walled CNT with stands a pressure upto 25 Gpa without deformation

3. Electrical properties :-
Because of symmetry and unique electronic structure of graphene, CNT is semi conducting with a very small band gap between valance band and conducting band. Because the electrons propagate only along the tube axis and involve quantum effects, CNT is reffered as one-dimensional conductor.

4. Thermal properties :-
CNT are very good thermal conductor and exhibit a property called ballistic conduction

→ Single walled CNT at room temprature has thermal conductivity 3500 $Wm^{-1}K^{-1}$ which is more than Cu metal (385 $Wm^{-1}K^{-1}$)

→ The temprature stability of CNT is 2800°C in vaccum and 750°C in air.

5. Toxicity :-

→ CNT possess toxicity

→ Under certain conditions CNT can ~~possess~~ cross the membrane barriers and reach organs which induces harmful effects inflammatory, fibrotic (toxicological changes in lungs) reaction and can cause cell death

* Applications of CNT :-

→ Because of the superior mechanical properties CNT's are used to make bullet proof clothing

→ used for producing CNT field effect transistors.

→ Because of their high conductivity CNTs are used for making nano-tube polymers composites which are used for making electrical cables and wires.

→ CNT can store hydrogen to be used as a fuel source.

→ Because of their strong UV/vis-NIR absorption characteristic it is used in solar panels

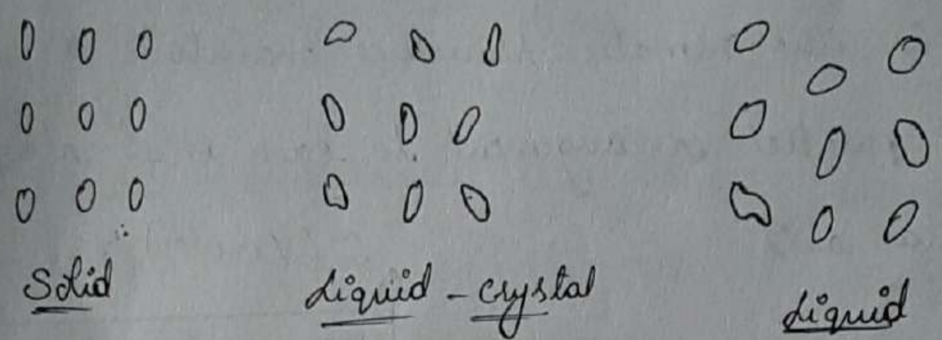
→ Used in cancer treatment

→ CNT can make waterproof and tear-resistant fabrics.

* Liquid crystals :-

→ Liquid crystals (LCs) are highly anisotropic fluids that exists between boundaries of the solid and isotropic liquid phase.

→ Liquid crystals have the fluidity of a liquid and can exhibit the optical properties of a solid



→ In liquid crystals the molecules are able to move, but not as much as they can move in liquid phase.

→ All the molecules in liquid phase tend to align along a common axis called director. This property is called anisotropy.

→ In liquid crystals, the orderly arrangement is sufficient to impart some solid like properties and at the same time the force of attraction between the molecules are not strong enough to prevent the flow

* Classification of liquid crystals :-

There are two types of liquid crystals

1. Thermotropic liquid crystals
2. lyotropic (~~LC~~) liquid crystals.

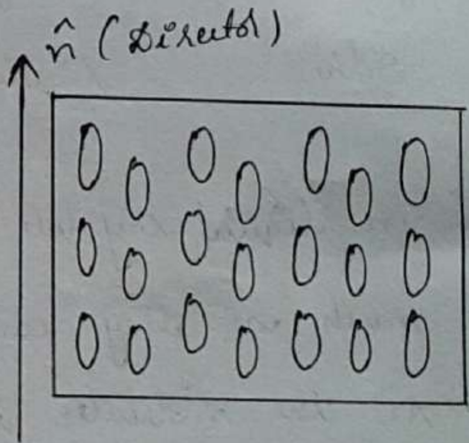
* 1. Thermotropic liquid crystals:-

→ These are formed only by the adjustment of the temprature

→ Thermotropic liquid crystals are further classified into (i) Nematic (ii) Cholesteric (iii) Smectic liquid crystals.

(i) Nematic liquid crystals :-

→ The molecules in the nematic structure maintain a parallel (or) nearly parallel arrangement to each other along the long molecular axis.



→ It is a one dimensional structure in which the molecule are mobile in three directions and rotate about one axis.

→ whenever the nematic structure is heated, it is generally transformed into the liquid

→ Even a dust particle can distort the nematic structure to liquid structure

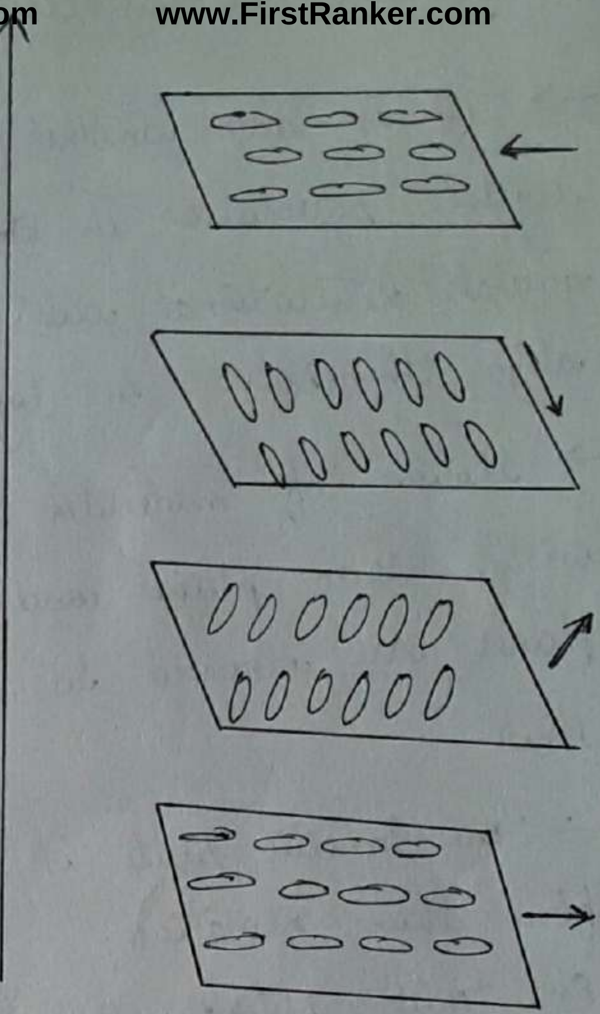
(ii) Cholesteric liquid crystals :-

→ These liquid crystals are formed by mesogenic molecules containing a chiral centre, which produces ~~their~~ inter molecular forces.

→ There inter molecular forces are responsible for alignment between molecules at a slight angle.

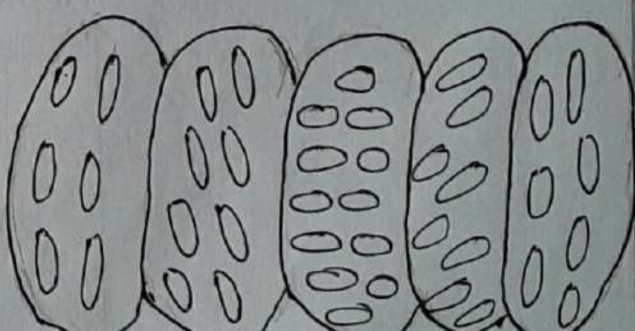
→ This structure appears as a stack of very thin nematic like layer in which the director is twisted with respect to above and below layers

→ As many compounds that forms this mesophase are derivatives of cholesterol, hence this structure is named is cholesterol liquid crystal phase.



* Pitch :- The pitch (P) is defined as the distance it takes for the directors to rotate one full turn in the helical structure.

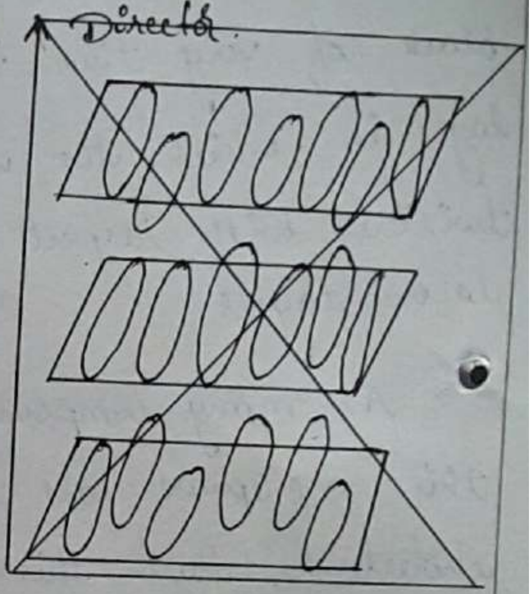
→ when the pitch length is equal to corresponding wave length of light in visible spectrum, then the liquid crystal reflects light of wavelength equal to pitch length.



→ Increase in the temperature of the molecule decreases the pitch length and vice-versa. Thus by identifying the reflected colour, we can determine the temp of a liquid crystal

Smectic (or) Smectic (structure) liquid crystals :-

→ It is also another distinct mesophase of liquid crystal substances in (the) which the molecule maintain the general orientational order of nematics, but also tend to align themselves in layers (or) planes

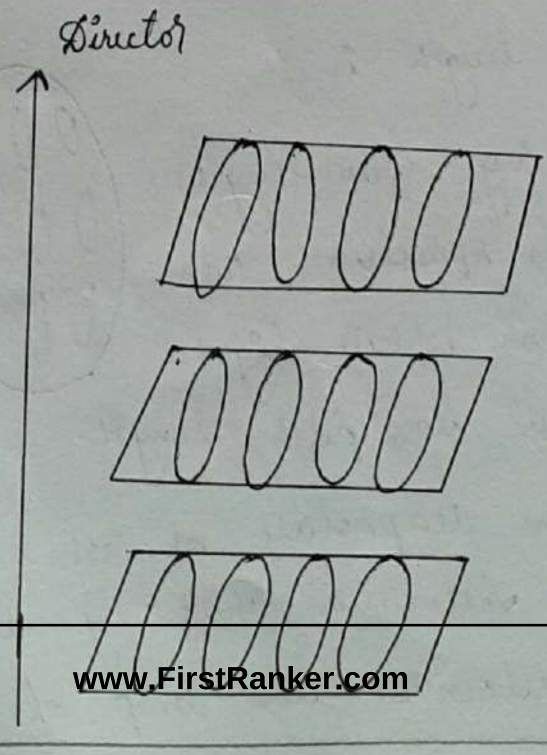


→ Motion of molecules is restricted within these planes and separate planes are observed to flow past each other

→ The smectic state is more solid like (form) than nematic.

Ex: Thick slippery substance often found at the bottom of soap dish.

→ There are several types of smectic structure labelled by the alphabet letters A to H. Some of them are

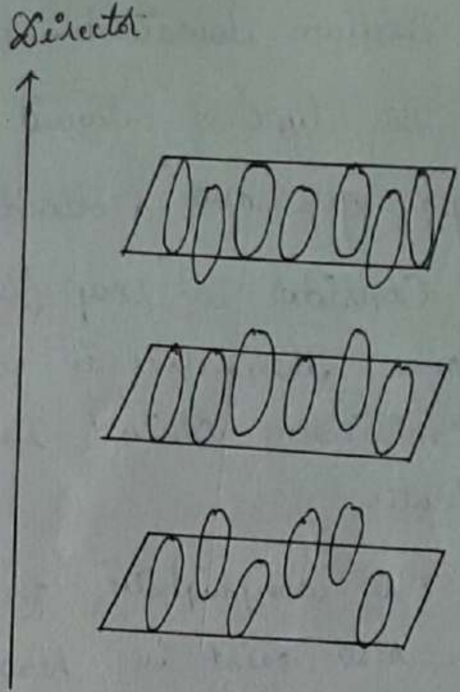


* Smectic - A :-

→ It is the least order phase of all the smectic structures.

→ The molecules in this phase are arranged in equally spaced layers with a definite repeated distance

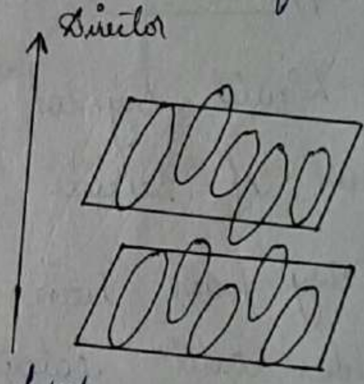
→ In this phase, long axes of the molecule is generally pependicular to the layer plane.



* Smectic - C :-

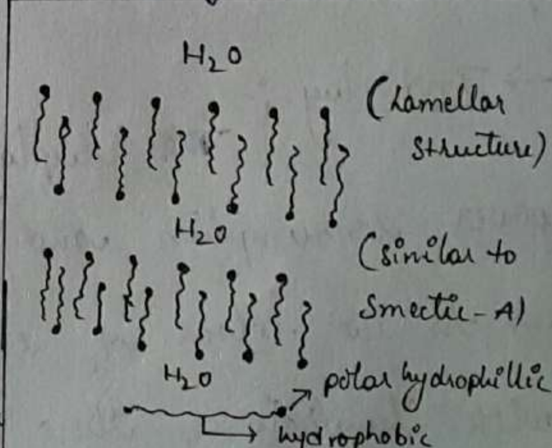
→ It is similar to that of section - A, except that of the molecule in the layers are tilted at a uniform angle with respect to the normal structure.

→ In this phase, the molecules are disorganised positionally and move about freely



* 2. Lyotropic liquid crystals :-

→ Some compounds are transformed to a liquid crystal phase, when mixed with solvent (or) when the concentration of one component is increased. Such component which exhibit liquid crystallinity on mixing with a solvent (or) changing its concentration are called lyotropic liquid crystals.

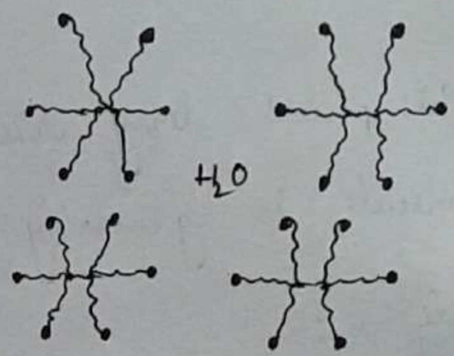


Ex: Sodium laurate in water

→ This type of liquid crystle phases are impotant in soaps, gels and colloids.

→ Consider a soap film, The amphiphillic soap molecules arrange themselves in a bilayer in water so that there is minimum contact between paraffic tails and the water molecules

→ The amphiphilic molecules can also exist in hexagonal phase, cubic phase etc



* Applications of liquid crystals :-

→ Liquid crystal technology is widely used in many areas of science and technology.

→ They have been used in temprature sensors, display for watches and calculators, high definition TV's and industrial products

→ In displays :- The display of these material runs with low power consumption and with a better charity.

→ As the colour of cholesteric liquid crystals changes with temprature, these can be used in the measurment of temprature. The cholesteric liquid crystal always

... is the same colour at the same temperature. The precise colour is very sensitive to changes in temperature using liquid crystle sensors, temperature variations of less than 0.01°c can be easily distinguised.

→ Nematic liquid crystals are useful in the application of NMR (Nuclear Magnetic Resonance). Samples that are dissolved in nematic liquid crystle solvents gives high resolution spectrum that can be used to identify the structure of sample.

→ Liquid crystal layers are used for stable monochromatic emmission.

→ Medical applications of liquid crystals are for studying circulatory system, detection of tumours, skin and ~~breast~~ (to) breast cancers.

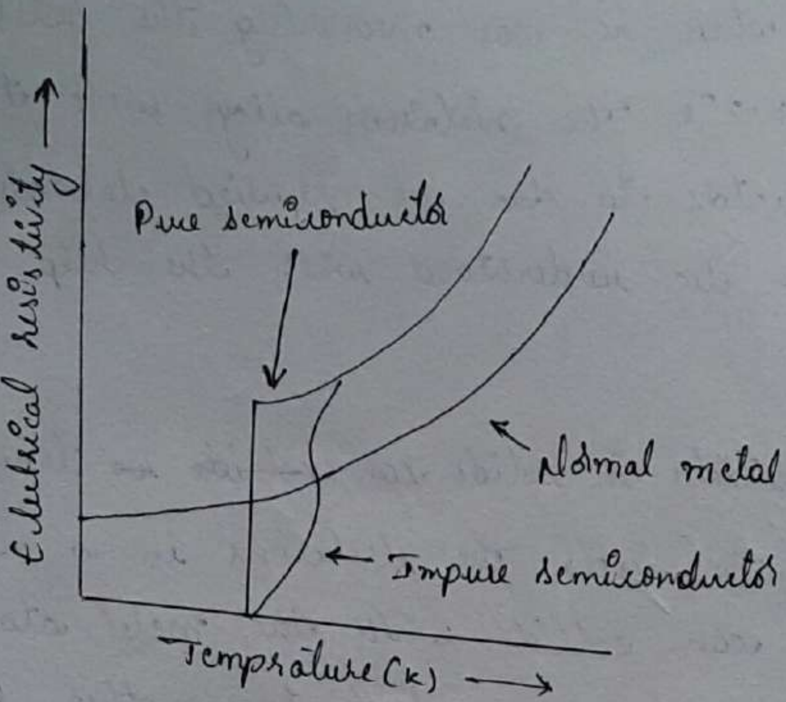
→ Liquid crystals are also used in finding the efficie-ncy of heat engines and testing of radiations.

Superconductors :-

A solid which offers no resistance to the passage of electricity through it, is called superconductor. The phenomenon was discovered by Dutch physicist kammerli-ngh onnes in 1911, when he was measuring the resistivity of mercury below 4.2°k. The niobium alloys were the earlist superconductors to be studied elaborately. Superconductivity can be understood with the help of quantum physics.

Charged particles in solids can (~~collide~~ ~~or~~) travel only in fixed direction or levels. The electrons in a normal metallic conductor can collide with the metal atoms and shift themselves from one level to another, but the electrons in a superconductor are prevented from such shifts by a unique quantum effect. These electrons are confined to their original level and therefore cannot collide with the atoms, and consequently must travel endlessly along fixed directions. Under such a circumst-ances, they head in one direction and continue to carry current endlessly

Superconductivity is exhibited by several metals, but only at low temperatures. The temperature at which the normal metal passes into superconducting state is called the superconducting transistion temprature (or) critical temp... denoted by T_c. The resistivity temprature behaviours for the superconductive and nonsuperconductive materials are differentiated below in the figure.



Types of superconductors :-

Superconductors are dived into two types based on their magnetic response.

(a) Type I (or) ideal superconductors

(b) Type II (or) Hard superconductors

Type - I superconductors are those which become completely diamagnetic in the superconducting state. These materials exhibit 'Meissner effect' i.e., the explusion of magnetic flux from the interior of a piece of superconducting (phase).

... as the material undergoes the transition to the super-conducting phase.

Type - II Superconductors are those in which the ideal behaviour is seen upto a lower critical (~~temprature~~) magnetic field beyond which the magnitization gradually changes and attains zero at an upper critical magnetic field.

* Yttrium barium cuprate ($YBa_2Cu_3O_{7-x}$ where x is small)

This functions as a superconductor at a critical temprature (T_c) of 90°K. The constituents of this material i.e, yttrium, barium and copper are in 1:2:3 molar stoichometric ratio and hence are called as 1:2:3 superconductors

* Synthesis of 1:2:3 superconductors by ceramic method

$YBa_2Cu_3O_{7-x}$ can be synthesised by solid state ceramic technique. This involves the following steps

(a) Preparation of a homogeneous mixture of there Oxides (Y_2O_3, $BaCO_3$ and CuO) in their molar ratioes

(b) Heating them to obatain oxygen deficient superconductor in a muffle furnance

(c) Annealing the above compound (b) to room temperature to retain its composition, structure and superconducting properties

* Classes of superconductors :-

Superconductors belong to different classes like

1) elements ⟶ Ex :- Hg, Nb, La
2) alloys ⟶ Ex :- La_3In, Nb_3Ge
3) Simple compounds → Ex :- NbN
4) molecular crystals → Ex :- $C_{60}K_x$
5) Non stachiometric crystals having defects → Ex :- TiO, NbO, $BaBi_{0.25}Pb_{0.75}O_3$
6) Ceramic ⟶ Ex :- mixed metal Oxides
7) Inorganic polymers ⟶ Ex :- $(SN)_x$
8) Organic compounds ⟶ Ex :- charge-transfer compounds between electron donors and electron acceptors. (like tetracyanoquinodimethane)

Properties of Superconductors:

1) Superconducting materials are generally brittle in nature. This property limits their ability to be fabricated into useful forms such as wires.

2) At room temperature, the resistivity of superconducting material is greater than other elements

3) A superconductor exhibits perfect diamagnetism. Because of diamagnetic nature, superconducting materials strongly repeal external magnets which leads to a levitation effects.

4) Thermoelectric effects of materials disappear in the superconducting state.

5) If the sufficiency of strong magnetic field is applied below T_c (superconducting transition temperature), its super-conducting property is destroyed

6) when current is passed through the superconducting materials, the heating loss i^2R is zero

[$\because$ Resistivity $\rho = 0$ at $T = T_c$;

$\therefore R = \rho l/A = 0$; $\therefore$ $i^2 R = 0$)

* Applications of Superconductors :-

1) Superconductors can be used to perform logic and storage functions in computers. Superchips made of superconductors for computers can function 1000 times faster than currently used silicon chips

2) Power can be transmitted through superconducting cables without loss as there is no I^2R loss in a superconductor.

3) A zero resistance combined with high current densities makes superconductors useful for strong electromagnets. They can be used for producing very strong magnetic field of about 50 tesla; which is much larger than the field obtainable from an electromagnet

4) Superconducting magnets capable of generating high field with low power consumption are currently employed in scientific and research equipment. They are used for magnetic resonance imaging (MRI) in the medical field as a diagnostic tool

5) Superconductors serve as gas sensors because their electrical resistivity sharply changes on contact with certain gases. For example $La_{2-x}Sr_xCuO_4$ is a good sensor for alcohol vapours.

Some superconductors function as excellent catalysts for industrial chemical processes. For example $YBa_2Cu_3O_{7-x}$ and the related cuprates act as catalysts in Oxidation & dehydrogenation reactions

7) More powerful magnets can be made with the help of Superconductors, which are likely to enhance the probability of laboratory nuclear fusion reactions

8) Superconducting magnets are employed for operating frictionless, high-speed leviating trains

9) Superconductors have very promising application as electronic filters. One possible use for these superconducting electronic filter would be in cellular Telephone systems, where it would allow more remote areas to be accessed

10) Superconducting material may be used in the manufacture of electrical generators and transformers in exceptionally small sizes having efficiency of 99.99%