

NON-ELEMENTAL SEMI CONDUCTING MATERIALS.

The materials which behave as insulator at absolute zero and conduct electricity at normal temperatures are called semiconductors.

→ This property of semi conductivity explained based on band theory.

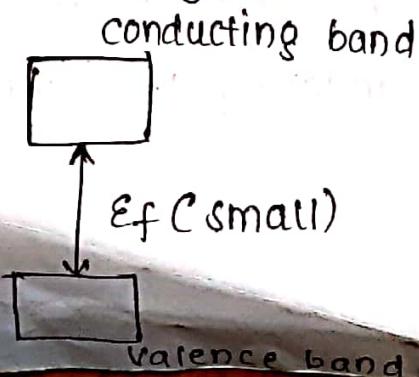
Types of Semiconductors.

* Semiconductors are two types.

1. Intrinsic Semiconductors

2. Extrinsic Semiconductors

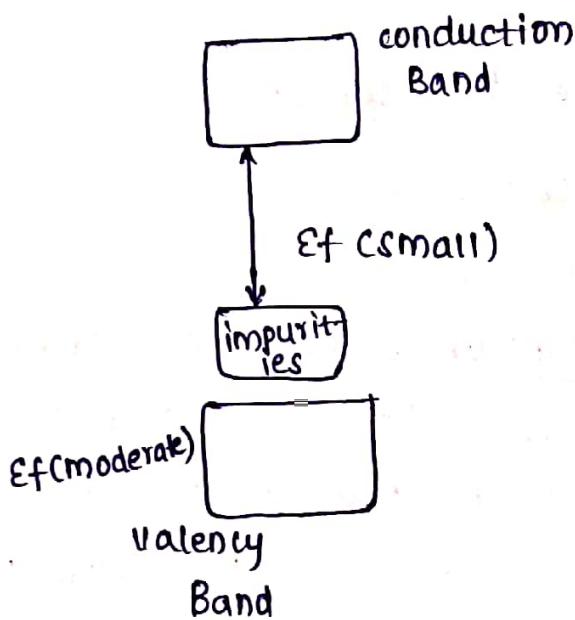
1. Intrinsic Semiconductors :- In the fermi energy gap is small b/w the Valence band and conduction band, so that the electron from valence band is excited to conduction band, it is called intrinsic semiconductor both the hole left in valence band and the excited electron to the conduction band contributes towards conductivity. As the temperature rises, the no. of electrons promoted to the conduction band increases contributing to the increase in conductivity of semiconductor.



2. Extrinsic Semiconductors :-

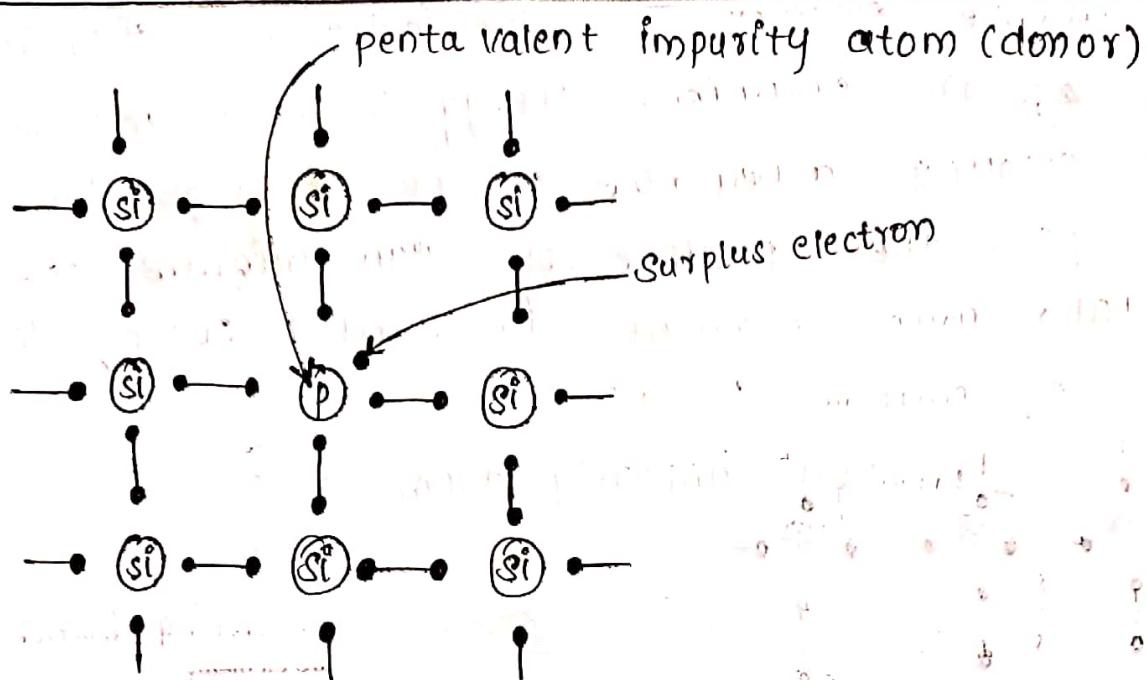
The fermi energy gap between valency band and conduction band is moderate in semiconductors is known as Extrinsic semiconductors.

* This gap is full-filled with impurities is known as doping.

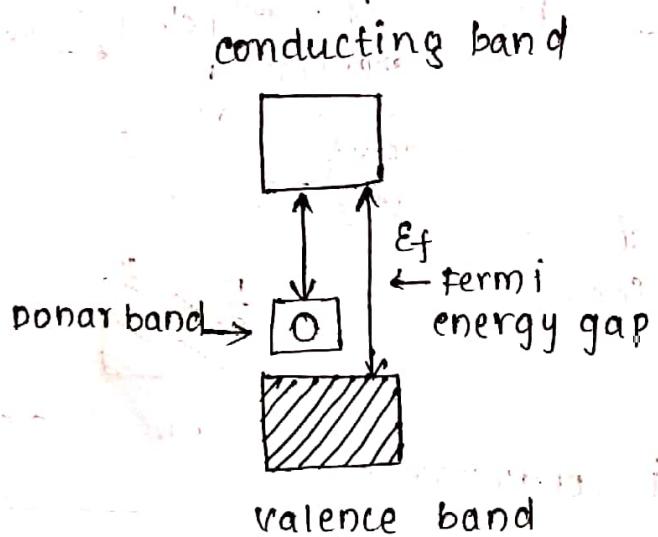


N-type Semiconductors :- The pentavalent impurities like P, As, to the silicon (or) Germanium semi conductors is known as N-type semiconductor.

* Pentavalent impurities have five electrons out of these four electrons bonded with Si (or) Ge, one surplus electron is wandering in semi conductors.



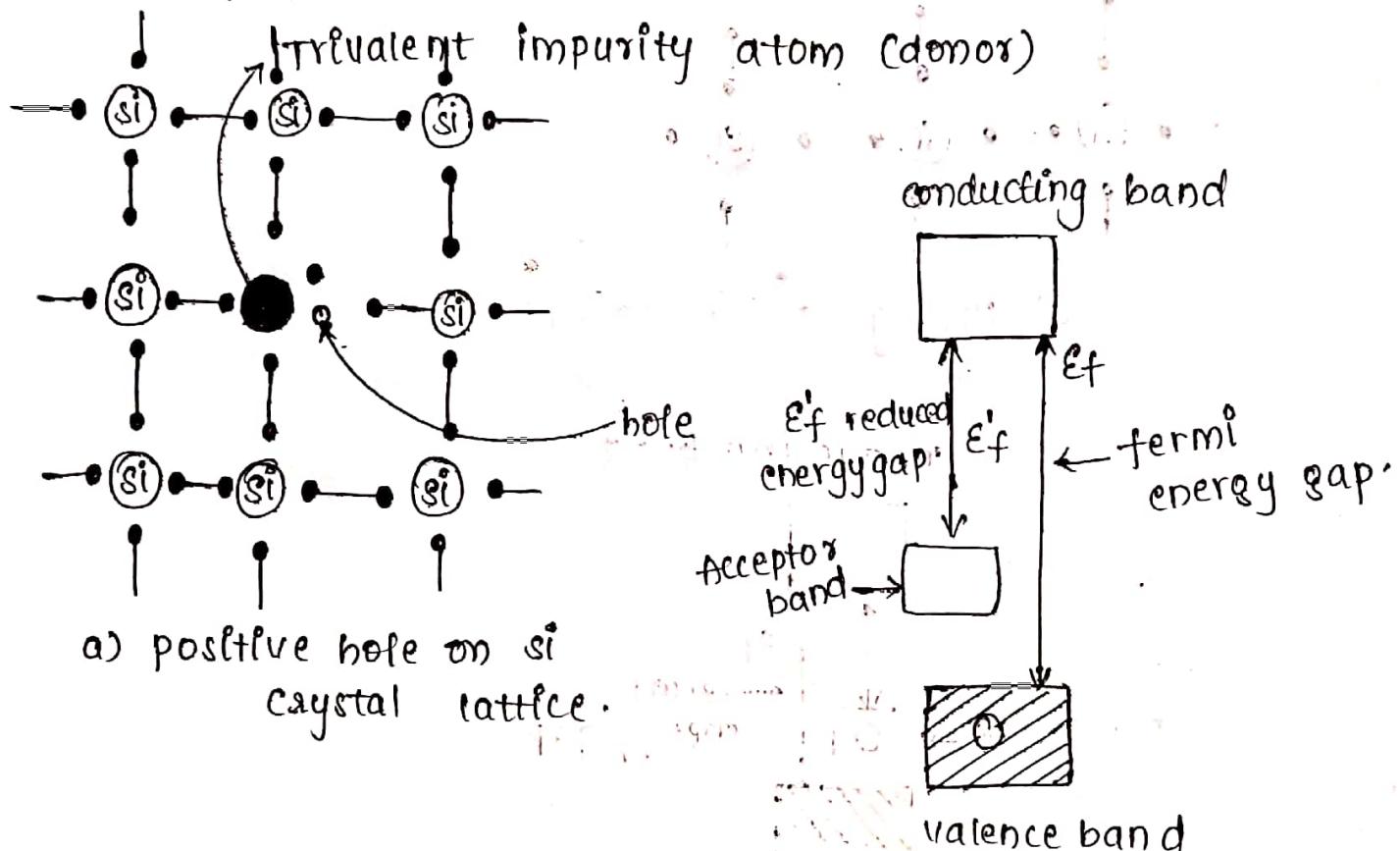
a) Doping of impurity



A dopant with more electrons form a narrow band.

P-type semiconductors:- By introducing a trivalent impurity atom like Al, B, Ga into Si or Ge, the replacement of these Si or Ge atoms by impurity produces an incomplete bond in the structure producing a positive hole. The positive holes are localized around trivalent impurity atom at low temperatures or absolute zero. At normal temperatures

the valence electrons on the adjacent Si or Ge atom may again sufficient energy to move into the hole, thus creating a new hole on the Si or Ge. By a series of hops, the positive hole can migrate across the crystal, thus current is carried out by the migration of positive centres.



Stoichiometric semiconductors:-

The crystal structures and band structures similar to that of silicon (Si) and Germanium (Ge) are developed by the combination of group III and group II elements and group-II and group-IV elements named as stoichiometric semiconductors.

Ex:-

Al₂O₃, Ga₂O₃, In₂O₃, SnO₂, ZnO, CdS, CdSe, CdTe, Cu₂S, Cu₂Se, Cu₂Te, Cu₃As, Cu₃Sn, Cu₃Ge, Cu₃Si, Cu₃Sn₂Ge, Cu₃Sn₂Ge₂, Cu₃Sn₂Ge₃, Cu₃Sn₂Ge₄, Cu₃Sn₂Ge₅, Cu₃Sn₂Ge₆, Cu₃Sn₂Ge₇, Cu₃Sn₂Ge₈, Cu₃Sn₂Ge₉, Cu₃Sn₂Ge₁₀, Cu₃Sn₂Ge₁₁, Cu₃Sn₂Ge₁₂, Cu₃Sn₂Ge₁₃, Cu₃Sn₂Ge₁₄, Cu₃Sn₂Ge₁₅, Cu₃Sn₂Ge₁₆, Cu₃Sn₂Ge₁₇, Cu₃Sn₂Ge₁₈, Cu₃Sn₂Ge₁₉, Cu₃Sn₂Ge₂₀, Cu₃Sn₂Ge₂₁, Cu₃Sn₂Ge₂₂, Cu₃Sn₂Ge₂₃, Cu₃Sn₂Ge₂₄, Cu₃Sn₂Ge₂₅, Cu₃Sn₂Ge₂₆, Cu₃Sn₂Ge₂₇, Cu₃Sn₂Ge₂₈, Cu₃Sn₂Ge₂₉, Cu₃Sn₂Ge₃₀, Cu₃Sn₂Ge₃₁, Cu₃Sn₂Ge₃₂, Cu₃Sn₂Ge₃₃, Cu₃Sn₂Ge₃₄, Cu₃Sn₂Ge₃₅, Cu₃Sn₂Ge₃₆, Cu₃Sn₂Ge₃₇, Cu₃Sn₂Ge₃₈, Cu₃Sn₂Ge₃₉, Cu₃Sn₂Ge₄₀, Cu₃Sn₂Ge₄₁, Cu₃Sn₂Ge₄₂, Cu₃Sn₂Ge₄₃, Cu₃Sn₂Ge₄₄, Cu₃Sn₂Ge₄₅, Cu₃Sn₂Ge₄₆, Cu₃Sn₂Ge₄₇, Cu₃Sn₂Ge₄₈, Cu₃Sn₂Ge₄₉, Cu₃Sn₂Ge₅₀, Cu₃Sn₂Ge₅₁, Cu₃Sn₂Ge₅₂, Cu₃Sn₂Ge₅₃, Cu₃Sn₂Ge₅₄, Cu₃Sn₂Ge₅₅, Cu₃Sn₂Ge₅₆, Cu₃Sn₂Ge₅₇, Cu₃Sn₂Ge₅₈, Cu₃Sn₂Ge₅₉, Cu₃Sn₂Ge₆₀, Cu₃Sn₂Ge₆₁, Cu₃Sn₂Ge₆₂, Cu₃Sn₂Ge₆₃, Cu₃Sn₂Ge₆₄, Cu₃Sn₂Ge₆₅, Cu₃Sn₂Ge₆₆, Cu₃Sn₂Ge₆₇, Cu₃Sn₂Ge₆₈, Cu₃Sn₂Ge₆₉, Cu₃Sn₂Ge₇₀, Cu₃Sn₂Ge₇₁, Cu₃Sn₂Ge₇₂, Cu₃Sn₂Ge₇₃, Cu₃Sn₂Ge₇₄, Cu₃Sn₂Ge₇₅, Cu₃Sn₂Ge₇₆, 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Cu₃Sn₂Ge₃₈₆, Cu₃Sn₂Ge₃₈₇, Cu₃Sn₂Ge₃₈₈, Cu₃Sn₂Ge₃₈₉, Cu₃Sn₂Ge₃₉₀, Cu₃Sn₂Ge₃₉₁, Cu₃Sn₂Ge₃₉₂, Cu₃Sn₂Ge₃₉₃, Cu₃Sn₂Ge₃₉₄, Cu₃Sn₂Ge₃₉₅, Cu₃Sn₂Ge₃₉₆, Cu₃Sn₂Ge₃₉₇, Cu₃Sn₂Ge₃₉₈, Cu₃Sn₂Ge₃₉₉, Cu₃Sn₂Ge₄₀₀, Cu₃Sn₂Ge₄₀₁, Cu₃Sn₂Ge₄₀₂, Cu₃Sn₂Ge₄₀₃, Cu₃Sn₂Ge₄₀₄, Cu₃Sn₂Ge₄₀₅, Cu₃Sn₂Ge₄₀₆, Cu₃Sn₂Ge₄₀₇, Cu₃Sn₂Ge₄₀₈, Cu₃Sn₂Ge₄₀₉, Cu₃Sn₂Ge₄₁₀, Cu₃Sn₂Ge₄₁₁, Cu<sub

Ex:-

Group III & V combination	Group II & VI combination
Semi conductor	fermi energy gap(E_f)
	(eV)
Gap	2.24
GaAs	1.35
Gasb	0.67
InAs	0.36
Cds	2.42
CdSe	1.74
Pbs	0.37

characteristics of stoichiometric semiconductors:

1. Stoichiometric semiconductors have wide energy gap, which leads to broad exhaustion zone with high conductivities. Hence they can be used at wider range of temperatures.
2. They can be doped to n or p-type semiconductors.

Non-stoichiometric semiconductors: The transition metal attached with chalcogen elements like oxygen to form two or more different semiconductor materials is known as non-stoichiometric semiconductors.

* In this type of semiconductor does not obey Arrhenius theory of electrolytic dissociation means the total no. of anions is not equal to total no. of cations.

Ex:- $\text{Fe} + \text{O} \rightarrow \text{Fe}_2\text{O}_3$

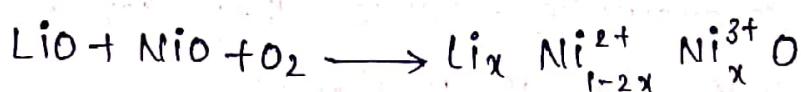
$\text{Cu} + \text{O} \rightarrow \text{CuO}, \text{Cu}_2\text{O}, \text{Cu}_3\text{O}$

$\text{Ti} + \text{O} \rightarrow \text{TiO}_2, \text{TiO}_3, \text{TiO}$

$\text{Mn} + \text{O} \rightarrow \text{MnO}, \text{Mn}_2\text{O}_3, \text{MnO}_4, \text{Mn}_2\text{O}_7$

Controlled valency Semiconductors.

$\text{Ni}_{0.7}^{2+} \text{Ni}_{0.2}^{3+} \text{O}$ is a hopping semiconductor producing hopping conductivity 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.



The semiconductor shows conductivities depending on temperatures and find applications as thermistors (thermally sensitive resistors). These semiconductors can be used over a wide range of temperature upto 200°C . The compound containing the composition $\text{Li}_{0.05}^{+} \text{Ni}_{0.9}^{2+} \text{Ni}_{0.05}^{3+} \text{O}^2$ is electroneutral semiconductor which is shown as below.

positive charge

$$\text{Li}_{0.05}^{+} = 0.05 \times 1 = 0.05$$

$$\text{Ni}_{0.9}^{2+} = 0.9 \times 2 = 1.8$$

$$\text{Ni}_{0.05}^{3+} = 0.05 \times 3 = 0.15$$

Negative charge

$$\text{O}^2 = 2$$

2

thus $\text{Li}_{0.05}^{+} \text{Ni}_{0.9}^{2+} \text{Ni}_{0.05}^{3+} \text{O}^2$ 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.

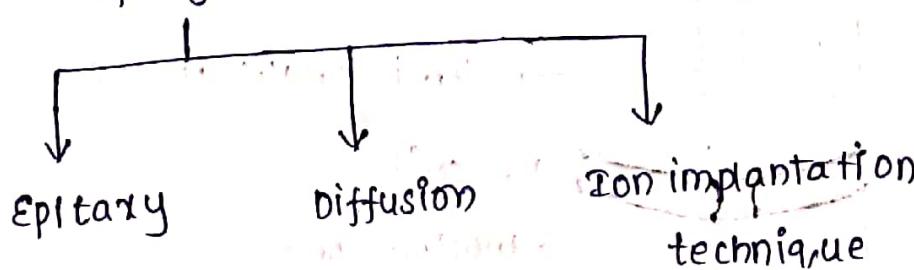
The characteristics of chalcogens are:

1. They behave as semiconductors or photo conductors either alone or by combining with other elements.
2. They rapidly form glass on cooling and viscous liquids on melting.
3. 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

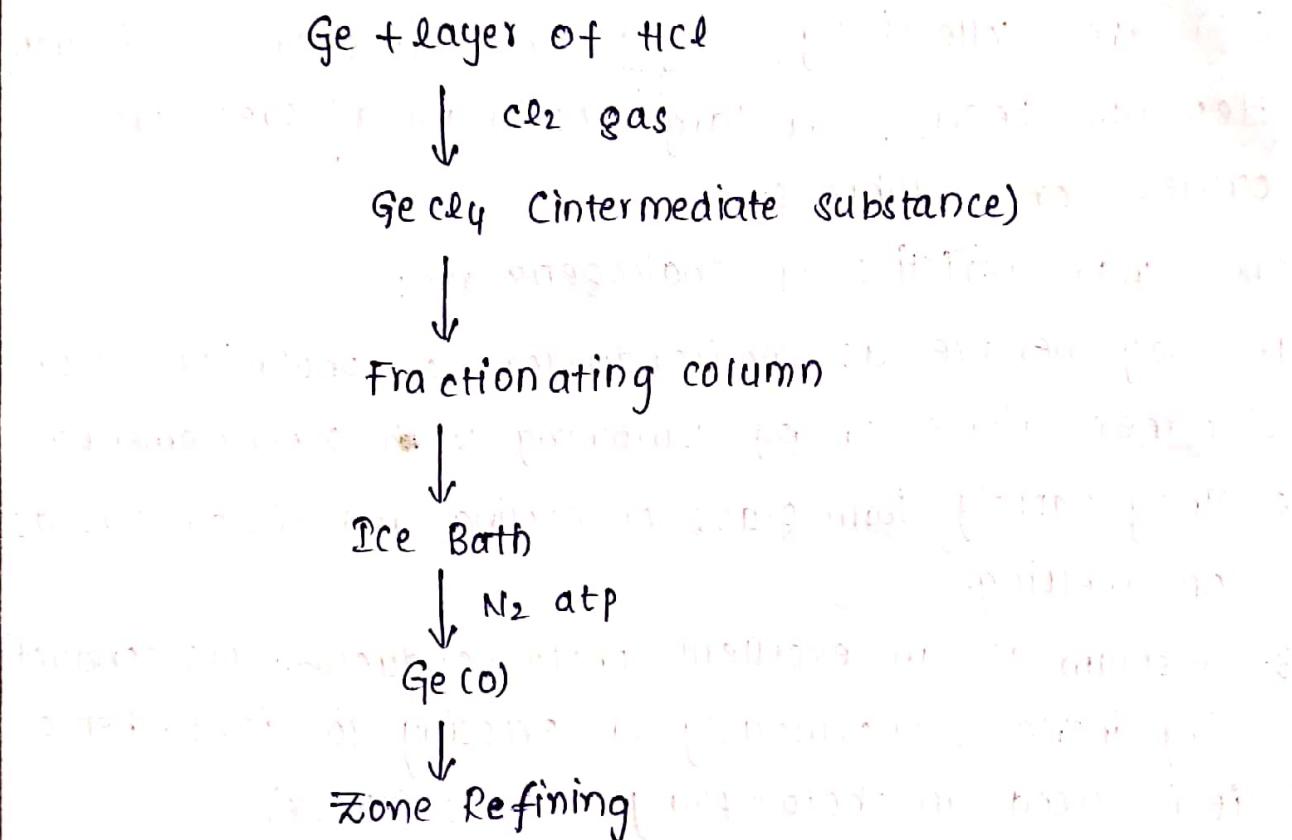
1. Preparation of ultra pure Ge → **distillation** → **Zone Refining**
2. Preparation of single crystals — **Czochralski crystal pulling technique.**

3. Doping

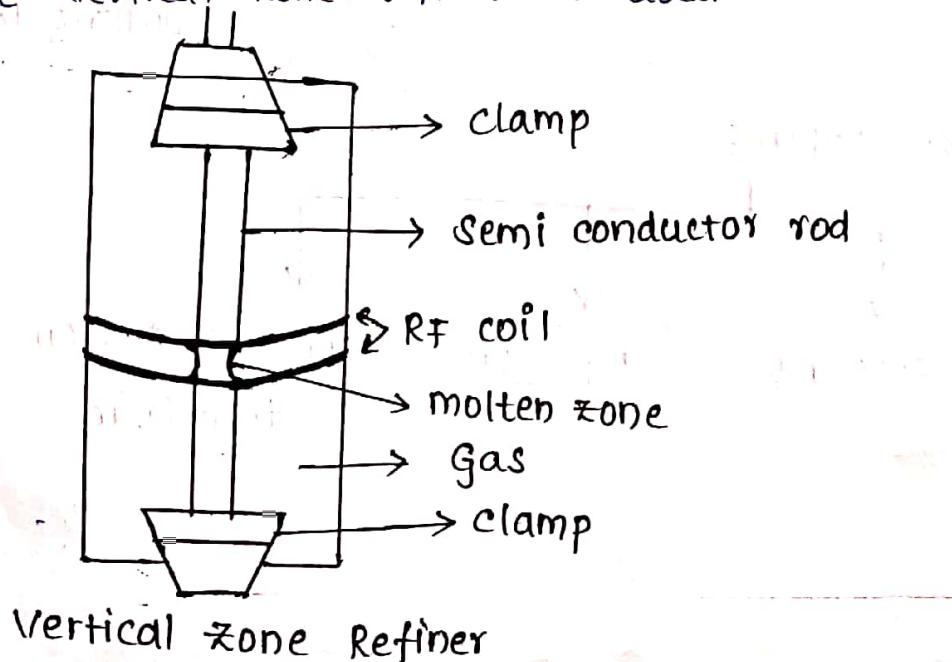


I. preparation of ultra pure Ge

a) distillation :-



b) Zone Refining :- Zone Refining is a metallurgical process which is based on the 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.



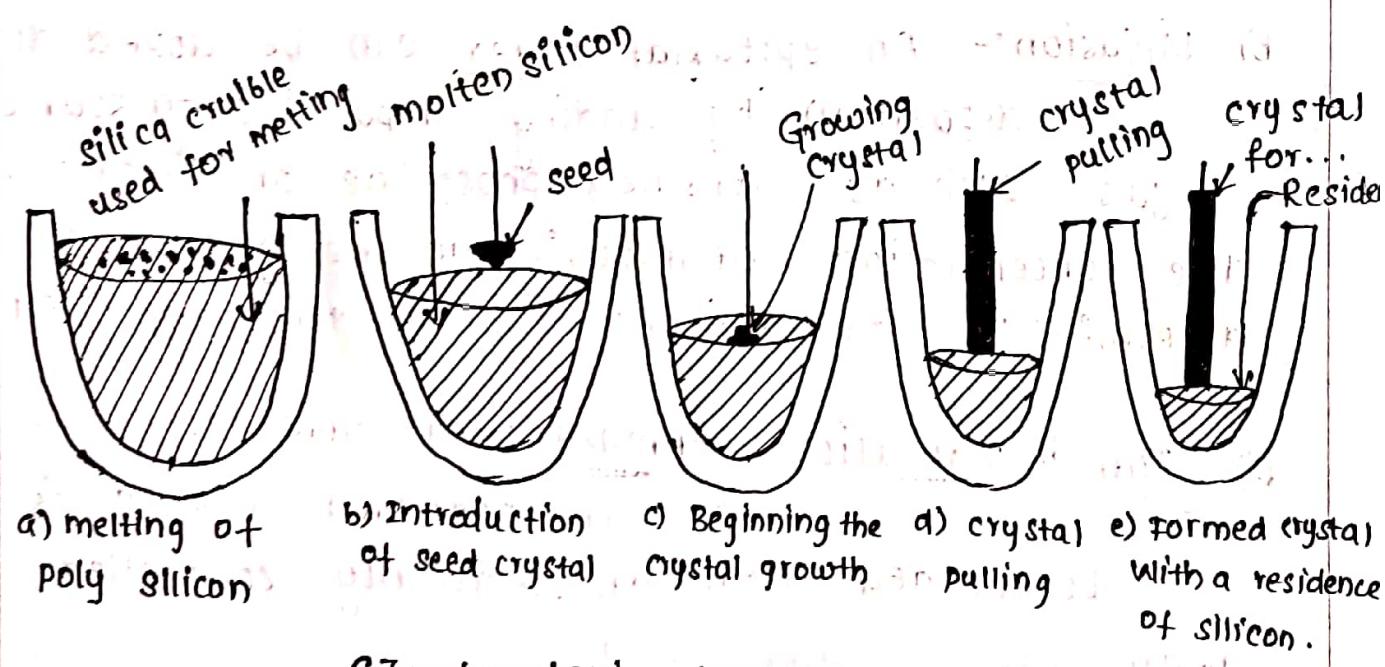
Q. Preparation of single crystals of Si or Ge:-

The basic requirement for the fabrication of a semiconductor device is that the semiconductor used must be a single crystal. Hence single crystal of Si and Ge are produced by Czochralski crystal pulling technique.

Czochralski crystal pulling technique:-

This process was named after the Polish scientist Jan Czochralski who invented the method in 1916 by accident while studying crystallization methods.

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.



Czochralski process.

3 Doping :- Introducing an impurity into the semiconducting crystal is called doping.

* One Boron (or) Arsenic atom added to 100 millions of Germanium (or) silicon.

a) Epitaxy :- The word 'Epitaxy' is derived from Greek, 'Epi' means several, 'taxy' means several manner. The deposition of a crystalline substance over the crystalline substrate. Epitaxy refers to the deposition of a crystalline over layer on a crystalline substrate which acts as seed crystal. The following are some of the techniques molecular beam epitaxy (MBE).

b) Diffusion :- An epitaxial layer can be doped during deposition by adding impurities to source gas such as arsine, phosphine or diborane. The concentration of impurity in the gas phase determines its concentration in the deposited film.

c) Ion implantation technique :- In this technique a semiconductor material is bombarded with an electrically controlled beam having higher energy of 10kev containing impurity ions like boron or phosphorous. Ion implantation method is extensively used in the fabrication of high frequency devices.

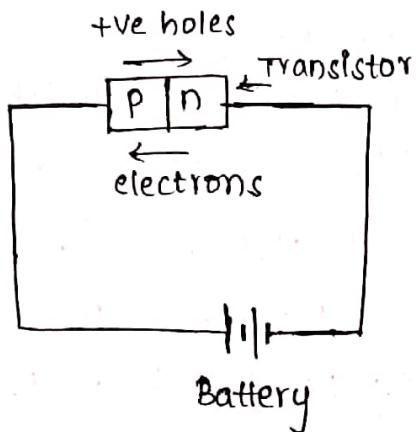
P-n Junction

When a single crystal of Si or Ge is doped with Indium at one end arsenic at the other end which constitutes one part p-type semiconductor and the other n-type semiconductor with middle boundary region where the two sides meet. This is known as p-n junction. The group III elements B, Al, Ga or In and group II element like P or As are mostly used because of their low melting point, which is useful for high temperature diffusion of the appropriate dopant element.

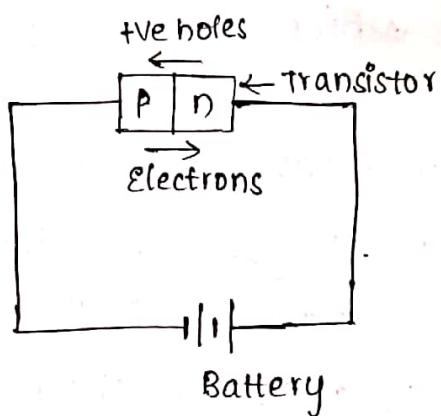
p-n Junction as a Rectifier:

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 (AC) to direct current (DC). The function of p-n junction as rectifier is discussed below. A transistor with two zones, one p-type and the 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 will migrate towards the p,n-junction, whereas holes will migrate towards the p-n junction. At the p-n junction of diode, the migrating electrons from the n-type region move into the vacant holes in the valence band of the p-type

region. This migration of electrons and holes can continue and a current flows as long as the external voltage than a battery P_s supplied.



a) conducts

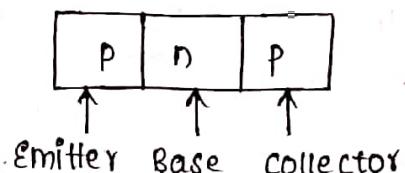
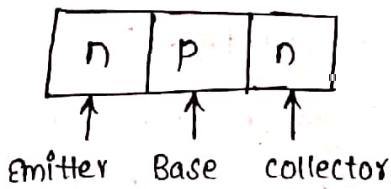


b) does not conduct

When the connection is reversed p-type region is connecting to the negative terminal of the battery and n-type region is connecting to the positive terminal of the 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 does not flow at the junction as there are no electrons or positive holes.

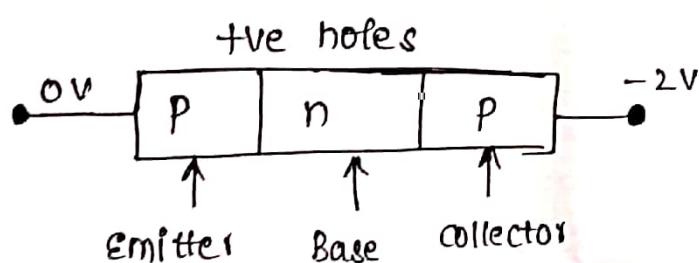
→ Junction transistors

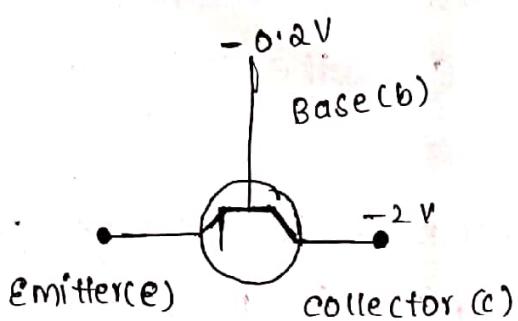
Transistors are single crystals of silicon which have been doped to give three zones, either p-n-p or n-p-n as shown below



Different voltages must be applied to the three regions of the transistor to make it work with respect to the emitter, the base is typically -0.1V and the collector is typically -2VOLTS .

In the p-n-p transistor, the charge carriers in the emitter are positive holes, which migrate from the emitter at 0V to the base at -0.1V . The positive holes cross the emitter/base p-n junction. In the n-type base region some holes combine with electrons and are destroyed. Electrons flow in the reverse direction from the base to the emitter. There is thus a small base current. Since the collector has much greater negative voltage and the base is very thin, most of the positive holes pass through the base to collector, where they combine with electrons from the circuit. At the emitter, electrons leave the p-type semiconductor and enter the circuit by producing more positive holes. Typically if the emitter current is 1mA , the base current is 0.02mA and the collector current is 0.98mA . Then 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 to the emitter.





Typical bias voltages for p-n-p transistor.

Applications of transistors :- Transistors are most widely used as:-

- I) Amplifiers and oscillators in radio, T.V, computers and hi-fi circuits , photo transistors , solar cells , detectors for ionizing radiations, thermisters and tunnel diodes.

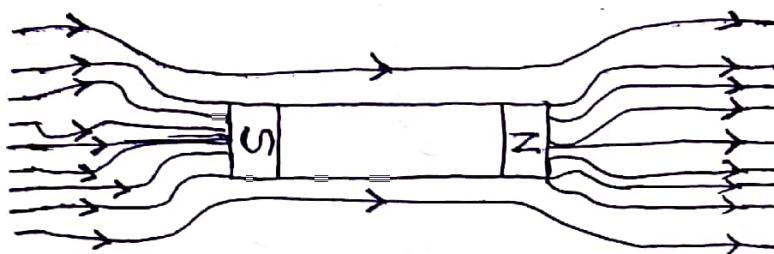
* MAGNETIC MATERIALS *

1) Ferro magnetism:

Ferromagnetic substances are those substances which are strongly attracted by a magnet.

Eg:- Iron, cobalt, Nickel, Gadolinium etc.

The lines of force tend to crowd into the Specimen.



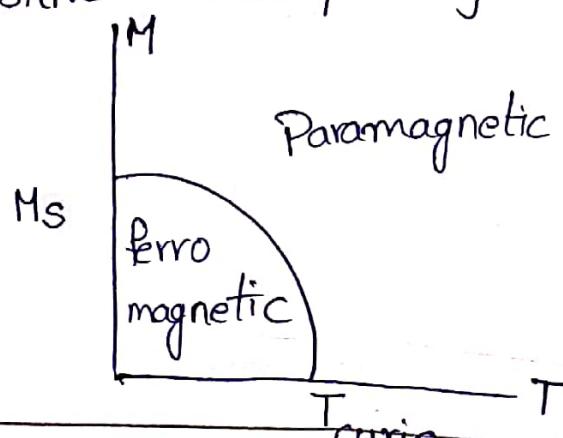
* It have spin (or) magnetic moment (or) dipole alignment. and also parallel and orderly alignment.

* Its behavior is heavy attraction of lines of force towards the centre.

* This magnetism having same direction as the External magnetic field.

* The permeability is very high.

* High positive susceptibility.



When temperature of the material is greater than its Curie temperature it is converted into paramagnet.

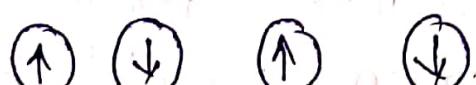
Application:

A common application for ferromagnetic materials is in the usage of data storage systems.

2) Ferri magnetism:

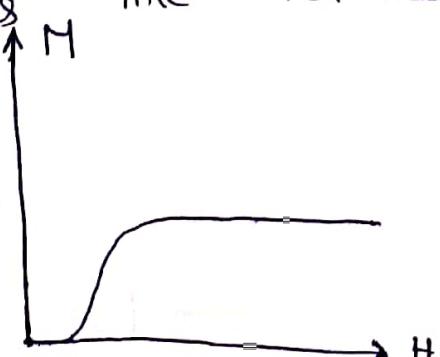
Ferri magnetic compounds observed in which have more complex crystal structure than pure elements like gold, silver, hydrogen, iron.

Atoms have mixed parallel and anti-parallel aligned magnetic moments.



Ferrimagnetic material are weakly attracted to ferro magnetic materials compared to ferri magnetic material.

Magnetic material can also classified as ferri magnetism although these are not observed in any pure elements. But these are found in mixed oxides like ferrites.



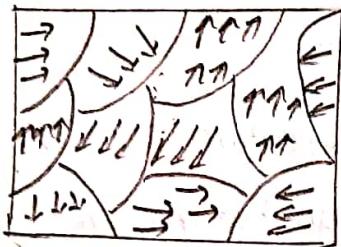
$M \rightarrow$ Magnetisation. Anisotropy & Remanence
 due to $H \rightarrow$ Influence on any applied
 and variable field. Relaxation time
Example: In Barium ferrite $[(2\text{BaO} \cdot 6\text{Fe}_2\text{O}_3)_2]$
 have 64 ions. out of these Barium and
 oxygen doesn't have magnetic moment. In this,
 we have 24Fe^{+3} ions in this 16Fe^{+3} ions
 undergoes parallel alignment and 8Fe^{+3}
 ions are anti-parallel alignment. and gives
 a net magnetisation parallel to the applied
 field.



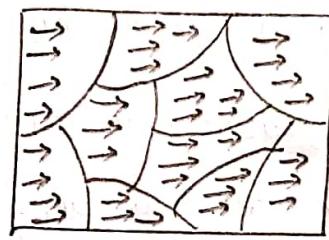
σ Saturation placed on iron in opposition
 to part of being opposite saturation nitrogen
 to iron in order and function magnetised
 towards the earth despite
 being the earth's magnetic field



Ferro magnetic Materials :- In some materials the permanent atomic magnetic moments have strong tendency to align themselves even without any external field. These materials are called ferro magnetic materials.



Before applying external field



After applying external field.

- Ferro magnetic materials are permanent magnets. means the material that can be magnetized by an external field and remain magnetized after the external field is removed.
- This is due to presence of domains : (domains are nothing but a group of atoms in that material). The domains have different direction of magnetic moments. So these moments shows magnetic property after removing external field (or) before applying the magnetic field.
- However, when we placed these material in external field domains are align in the direction of magnetic field. materials shows large magnetic property even the small magnetic field is applied due to domains.

Retentivity :- The value of magnetic induction B left in the material, when the small magnetising force H is removed. this is known as "Retentivity (or) Remanence"

→ Retentivity become zero. By applying two methods.

i) coercivity

ii) curie temperature

Coercivity : To reduce the retentivity to zero, we have to apply a magnetising force in opposite direction this value in magnetising force is called coercivity.

Curie temperature : Temperature is inversely proportional to the magnetising force. We apply the temperature (or) heating the material at a certain temperature retentivity become zero. That temperature is called curie temperature.

Every substance has its specific curie constant 'c'.

→ magnetic susceptibility is inversely proportional to absolute temperature.

$$\chi = \frac{C}{T - T_c}$$

χ = magnetic susceptibility

c = material specific Curie constant

T = absolute temperature

T_c = Curie temperature.

Hysteresis curve : The curve represent the relation between Intensity of magnetization (I) of a ferro magnetic material with magnetic intensity (H) is called hysteresis curve.

Electrical Insulators

Insulators :-

The substance which are capable of opposes or resists the flow of heat (or) electricity (or) sound through them are known as "insulators"

Insulators can be classified into 3 types

- 1) Thermal Insulators
- 2) Sound Insulators
- 3) Electrical Insulators

Electrical Insulators :-

The materials which are capable of opposes/ resists the flow of electricity through them are known as "Electrical Insulators"

$$\boxed{E = C/C_0}$$

C = Capacitance of system in material inserted

C_0 = Capacitance of system with vacuum between the capacitor plates.

Characteristics of Electrical Insulators :-

A good Electrical Insulators should possess

- low electrical conductivity and high resistivity
- low dielectric constant
- low porosity
- Chemical inertness towards acids, Alkalis, Solvents

These Insulators after Electrical can be classified into the three types

* Gaseous Insulators

* Liquid Insulators

* Solid Insulators

Gaseous Insulators :-

The best Examples of gaseous Insulators Air, Nitrogen, Hydrogen etc.

Air :-

Properties :-

→ Most important of all dielectric gases

→ It acts as a reliable insulating material when voltage are not very high

Applications :-

→ It provides insulation between overhead transmission lines without any cause.

Nitrogen :-

Properties :-

→ It is chemically inert dielectric

Application :-

→ used in transforms and Capacitors

Liquid Insulators:-

1) Mineral oils:-

Properties:-

→ These are obtained from crude petroleum

→ These are used in temperature range of 50°C to 110°C

Application:-

→ These are used in capacitors, switch gases etc.,

2) Askarles:-

→ These are highly inflammable synthetic insulating liquids used in temperature range 50°C to 110°C

Application:-

→ These are used as transformer liquid

Solid Insulators:-

Paper & press boards:-

Property:-

→ These are strong and more heat resistant

Application:-

→ These are used for windings and cable oil insulator

polystyrene:-

Property:- It passes excellent di-electric properties

Application:- It is used as insulators in high-frequency capacitors, telephones etc.,

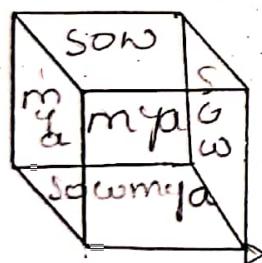
B. CHEMISTRY OF ADVANCED MATERIALSNANO MATERIALS:

(1)

The materials like metals, ceramics, polymeric materials or composite materials with dimensions and tolerances in the range of 1nm to 100nm are called the Nano materials. They exhibit unique properties like melting point reactivity, reaction rates, electrical conductivity, colour, transparency etc.

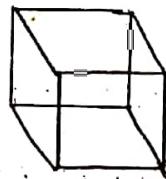
GENERAL METHOD FOR PREPARATION OF NANO MATERIALS:1. TOP-DOWN APPROACH METHOD:

In this method bulk materials are converted to powder and then to nanoparticles by making use of lithographic methods. This method is used in the microelectronic industry.



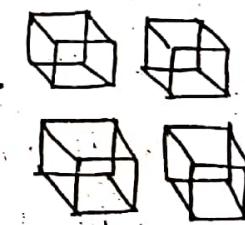
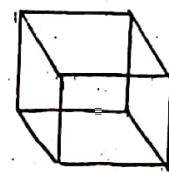
BULK

lithographic
method



POWDER

lithographic
method

NANO
PARTICLES2. BOTTOM-UP APPROACH METHOD:

In this method very small particles like atoms are assembled to get clusters which in turn are aggregated to get nanoparticles. Fullerenes and polymer nano composites are prepared by this method.



ATOMS



CLUSTERS

Aggregated



NANO PARTICLES

PREPARATION OF NANOMATERIALS BY INDUSTRIAL METHOD

1. SOL-GEL METHOD:

Sol-gel preparation is bottom-up approach for the synthesis of nanomaterials. Sol-gel processing is wet chemical technique that uses a sol to produce an integrated network i.e., gel. Metal oxides or metal chlorides undergoes hydrolysis and poly-condensation reactions to form a colloid which is a system composed of nano particles dispersed in a solvent. The solvent evolves toward the formation of an inorganic continuous network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centres with $\text{O}_\text{XO}(\text{M}-\text{OM})$ or hydroxo polymers ($\text{M}-\text{OH}-\text{M}$) bridges generating metal-oxo (or) metal-hydroxo polymers in the solution. After drying process, liquid phase is removed from gel and calcination is performed. Alcohol is used as solvent.

Advantages:

- It forms similar size of nanomaterials
- It undergoes low temperature reactions
- It forms microstructure particles
- It controls any stage of the reactions.

2. CHEMICAL REDUCTION METHOD:

This method belongs to bottom-up approach. Metal nanoparticles particularly silver nanoparticles are prepared by this method.

Preparation of silver nanoparticles:

For the preparation of silver nanoparticles

Silver nitrate solution and 8% w/w sodium dodecylsulphate (SDS) are used as metal salt precursor and metal stabilizing agent respectively. Hydrazine hydrate and citrate solution are used as reducing agents. The transparent colourless solution will be ⁽²⁾ converted to pale yellow and pale red colour which indicates the formation of silver nanoparticles. The nanoparticles are purified by centrifugation.

Applications:

→ Nanoparticles like silver, gold, platinum etc., are prepared by this method.

3. BEUNAR EMMET TELLER METHOD (BET):

Nano crystalline particles of " $\text{Co}_x \text{Fe}_{(3-x)}\text{O}_4$ " are synthesized by combustion reaction method using iron nitrate, cobalt nitrates and urea with Asa's fuel without template and subsequent heat treatment. The maximum reaction temperature range is 850 - 1010°C and combustion lasts for 30 sec. for all system. The materials are washed with deionised water and the byproducts are rinsed off producing pure nanoparticles.

4. TRANSMISSION ELECTRON MICROSCOPIC METHOD (TEM):

This is a shape controlled method for the synthesis of colloidal platinum nanoparticles which is potentially important in the field of catalysis. A solution of potassium platinum chloride solution (0.00001M) is prepared in water and treated with 0.2ml of 0.1M sodium polyacrylate. The resulting solution is bubbled with Ar gas for 20 min. The Pt ions are reduced by bubbling hydrogen gas for 5 min. The reaction vessel is sealed and left overnight. The solution turns light golden and nanoparticle

are purified and separated.

PROPERTIES OF NANOMATERIALS:

- The magnetic properties increases with decrease in size of materials.
- Melting point of the nanomaterials increases when compared with other material depending on size of particles
- Solubility of nanomaterials is more than other materials due to decreased size.
- Colour : The physical property colour is again size dependant.
- Transparency : Transparency of nanomaterials is more than other materials.
- Catalytic Behaviour: Due to increased surface area, the catalytic activity of the nanomaterials is more than other materials.
- Colloidal properties : The colloidal nanoparticles are called coexisting colloids.
- Chemical Reactivity : Nanoparticles posses high chemical reactivity
- Reaction Rates: High reaction rates were observed with nanomaterial.
- The nano materials exhibit good dispersibility
- The nanomaterials can be used as good conducting, semi-conducting and insulating materials.

FULLERENES:

A fullerene is any molecule composed entirely of carbon in the form of a hollow sphere, ellipsoid or tube.

The first fullerene molecule was prepared in 1985 by "Richard Smalley et al" at Rice University, USA. They were awarded Nobel Prize in 1996 for their work. (3)

TYPES OF FULLERENE:

1. BUCKYBALL CLUSTERS:

The smallest is C_{20} (unsaturated version of dodecah-drene) and most common is C_{60} .

2. CARBON NANOTUBES:

Hollow tubes of very small dimensions having single or multiple walls.

3. MEGATUBES:

Larger in diameter than nanotubes and prepared with walls of different thickness.

4. POLYMERS:

Chain, two dimensional and three dimensional polymers are formed under high-pressure, high-temperature.

5. NANO ONIONS:

Spherical particles based on multiple layers surrounding a buckyball core proposed for lubricants.

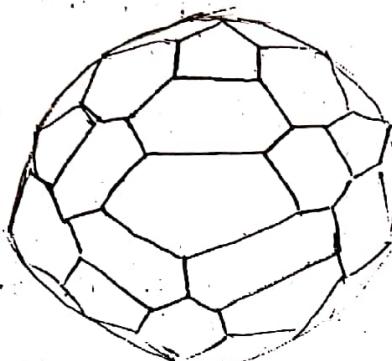
6. LINKED BALL AND CHAIN DIMERS:

Two buckballs linked by a carbon chain. The different individual fullerenes based on composition is listed below.

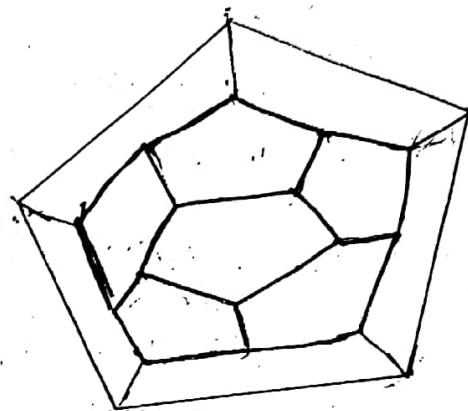
a, BUCKMINSTER FULLERENE:

It is the smallest fullerene molecule. The structure of C₆₀ is called "Truncated Icosahedron" containing 20 hexagons and 12 pentagons with carbon atom at the vertices of each polygon. The van der waals diameter of C₆₀ is 1.1 nm and average bond length is 1.4 Å.

12-Pentagonal rings
20-hexagonal rings



C₆₀ fullerene



C₂₀ fullerene

b, BORON BUCKYBALLS:

A type of buckyball which uses boron atoms instead of a carbon atom is Boron fullerene.

c, METALLO FULLERENES:

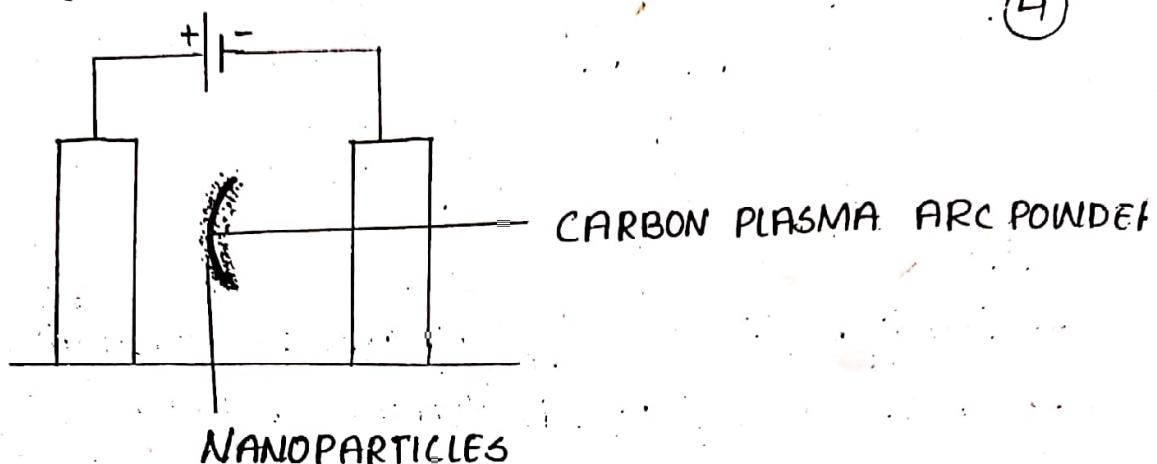
These are a class of novel nanoparticles, comprises 80 carbon atom (C₈₀) forming a sphere which encloses a complex of three metal atoms and one nitrogen atom.

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.

(4)



PROPERTIES OF FULLERENES:

→ Endohedral Fullerenes:

When other atoms tapped inside fullerenes to form inclusion compounds is known as endohedral fullerenes.

Eg: Tb_3NeC_{84} (Egg shaped fullerene).

→ Solubility:

Fullerenes are sparingly soluble in many solvents, common solvents for fullerenes are toluene, C_5 ,

→ Ceramic sculptures:

Several sculptures symbolizing wave-particle duality are created.

→ Chirality:

Some fullerenes are inherently chiral because they are D_3 -symmetric and have been successfully resolved.

→ Hydrogenation:

C_{60} exhibits a small degree of aromatic character, undergo addition with hydrogen to polyhydrofullerenes.

→ Halogenation:

Addition of F, Cl and Br occur for C₆₀ under various conditions, produces a vast no: of halogenated derivatives.

→ Addition of oxygen:

C₆₀ can be oxygenated to epoxide C₆₀O.

Applications:

- Buckyballs are efficient medium to make hydrogen fuel
- In medical field, buckminsterfullerene is used to inhibit the HIV virus
- It is used in preparation of solar energy.

CARBON NANOTUBES (CNT):

Carbon nanotubes are sheets of graphite about 0.4nm in diameter. Carbon nanotubes are otherwise called bucky tubes

There are two types of carbon nanotubes

1. Single Wall nanotubes
2. Multi Wall nanotubes

PREPARATION METHODS OF CARBON NANOTUBES

i, Arc Discharge Method:

By arc discharge of graphite electrodes in presence of ionised gas to reach high temperature and by using a current of 100 amps CNT was produced. The yield is 30% and produces both single and multi-walled nanotube with lengths of upto 50 micrometers.

iii, LASER ABLATION:

In this process a pulsed laser vapourises a graphite target, in a high temperature reactor. While an inert gas is bled into the chamber, nanotube develops on the cooler surface of the reactor as the vapourised carbon condenses. To improve the yield a composite of graphite, metal catalyst particles (Co and Ni mixture) was used to synthesis single walled CNT.

iii, PLASMA TORCH METHOD:

Single walled CNT was prepared by this method. In thermal plasma torch method high frequency oscillating currents in a coil in flowing inert gas was fed with feed stock of carbon black and catalyst particles and then cooled down to get single walled nanotubes. This method produces 2 gms of CNT per minute.

iv, CHEMICAL VAPOUR DEPOSITION (CVD):

During chemical vapour deposition process a substrate was prepared with a 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 carbon containing gas is broken and carbon is transported to the edges of the particle where it form CNT. Fluidised bed reactor is most widely used for CNT production.

PROPERTIES OF CNT:

→ Strength:

CNT possess strength upto 100 gigapascals (GPa)

→ Hardness:

Standard single walled CNT withstands a pressure upto 25 GPa without deformation

→ Kinetic Properties:

Multiwalled CNT exhibit a striking telescoping property

→ Electrical properties:

CNT is semiconducting with a very small band gap between valence band and conducting band.

→ Electromagnetic wave absorption:

CNT possess microwave absorption characteristic

→ Thermal properties:

CNT are very good thermal conductor, CNT at room temperature has thermal conductivity $3500 \text{ W M}^{-1} \text{ K}^{-1}$. The temperature stability of CNT is 2800°C in vacuum & 750°C in air.

→ Toxicity:

CNT possess toxicity.

Applications of CNT:

→ CNT's are used to make space elevators, stab-proof, bullet-proof clothing

→ CNT is used in paper batteries

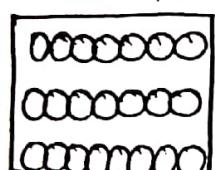
→ Used in digital switching devices, electromagnetic wave detectors.

- CNT can store hydrogen
- Single walled CNT is inserted around cancerous cell, hence used in medical field.

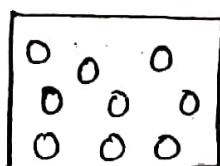
(6)

Liquid Crystals (LCS):

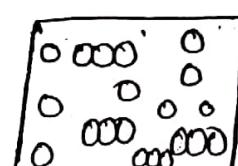
The substances which exhibits conventional liquid properties as well as crystalline solid property is called liquid crystals.



SOLID



LIQUID



LIQUID CRYSTALS

Types of liquid crystals:

1, Thermotropic LCS

2, Lyotropic LCS

3, Metallotropic LCS

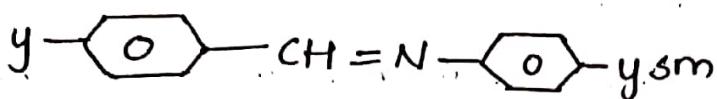
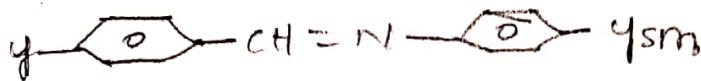
Thermotropic LCS:

Thermotropic phases are those that occur in a certain temperature range. Examples of thermotropic liquid crystalline substances are cholesteryl benzoate, exhibit liquid crystalline state $145.5 - 178.5^{\circ}\text{C}$, P-azoxyanisole at $116 - 135^{\circ}\text{C}$, and P-azoxyphenetole at $137 - 167^{\circ}\text{C}$.

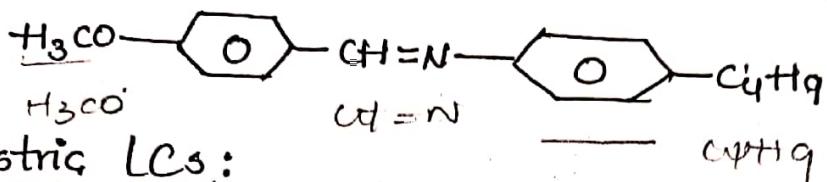
There are three distinct phases in which thermotropic LCS exists.

a) Nematic liquid phases:

Nematic in Greek means thread like simple structures



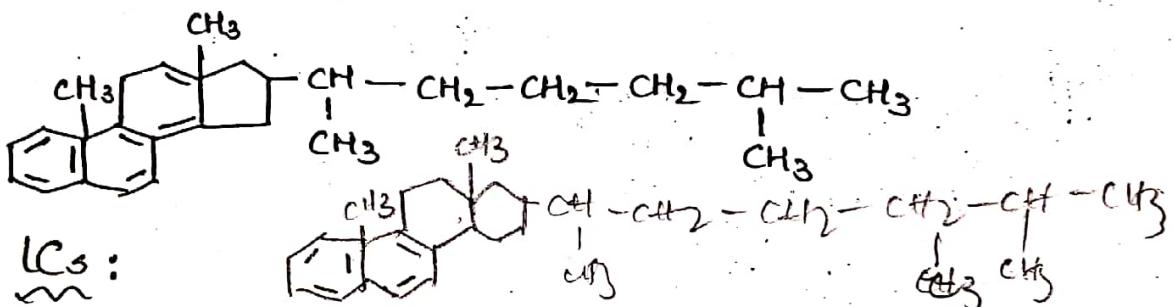
Example:



b, Cholestric LCs:

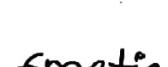
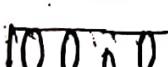
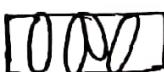
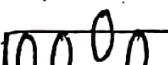
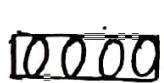
The molecules are aligned parallel to a preferred direction as in nematic phase. When proceeding in a direction normal to the plane, the preferred direction rotates continuously, the result is helical structure.

Example:



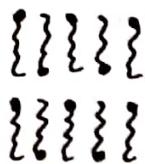
c, Smectic LCs:

In greek smetic means soap. There are three types of smetic phases based on orientation of the director.

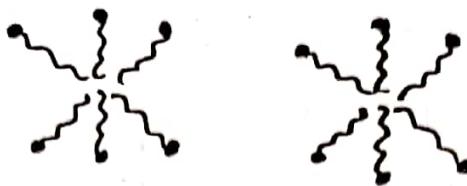


Lyotropic LCs:

Whenever the substance is added to liquid crystals it will increase the concentration of liquid crystal phase is called Lyotropic LCs.



LAMELLAR LYOTROPIC LCs

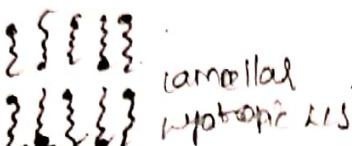


HEXAGONAL LYOTROPIC LCs

(7)

APPLICATIONS:

- Preparation of LCD TV's, laptops, computer monitors
- It is used in inhibition of cancer cells, tumour cells
- Used in aquariums
- Used in electromagnetic wave detectors.



Lamellar
Lyotropic LCs

SUPER CONDUCTORS:

The scientist Dutch physicist "Kamerlingh Onnes" in 1911 proposed super conductors.

A solid which offers no resistance to passage of electricity through it is called super conductors.

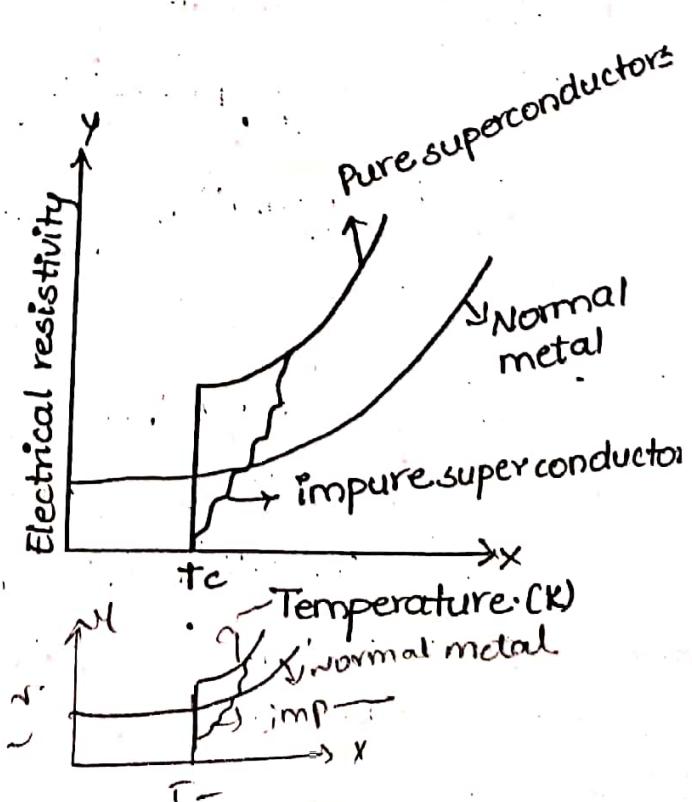
Types of superconductors:

i. Type-I superconductor (or)

Ideal superconductor:

→ In this superconductor, it exhibits diamagnetic property and also meissner effect.

→ The critical temperature (T_c) is high when compared to normal temperature (T)



Super critical fluid extraction method :-

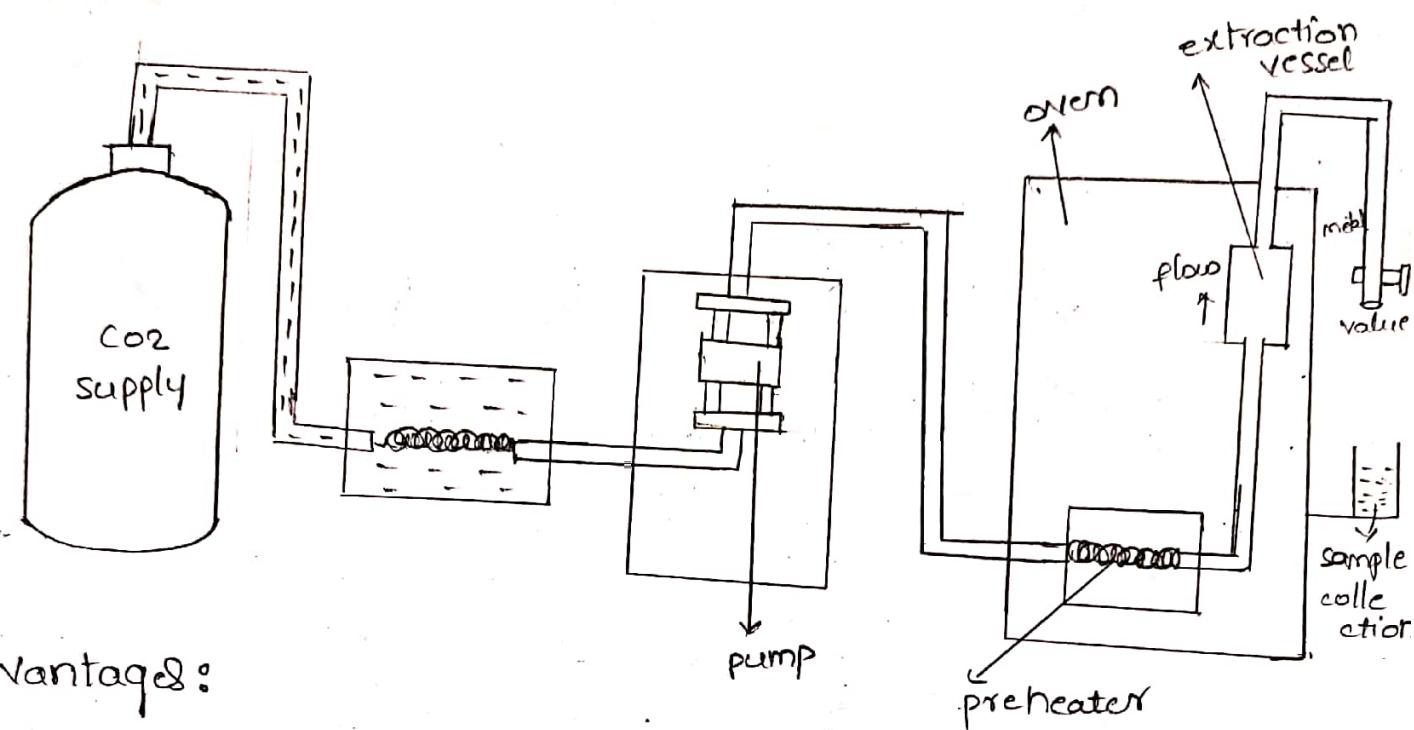
1. SFE is the presence of separating of one component from another component using super critical fluid as the extracting solvent extraction is usually from a solid matrix but can also be from liquids
2. SFE method is used for analytical purpose on a large scale to either unwanted material from a product (de-caffination) or collect a desired product (essential oils)
3. These essential oils can include limonene ($C_{10}H_{16}$) (terpene type of hydrocarbon) and other straight solvents
4. Carbon dioxide (CO_2) is the most used super critical fluid some time co-solvents such as methanol and ethanol

conditions of SFE :-

1. In SFE method, we use CO_2 undergoes critical temperature above of $31^\circ C$ and critical (temperature) pressure is 74 bar $7 \text{ bar} = 10^5 \text{ pascal}$

Procedure :-

The system must contain a pump for the CO_2 a pressure cell contain sample. we apply a pressure cell contain sample. we apply pressure in the system and a collecting vessel. The liquid is pumped to a heating zone where it is heated to super critical condition. it then passes into extraction vessel where it rapidly diffuses into solid matrix and dissolve the material to be extracted.



advantages:-

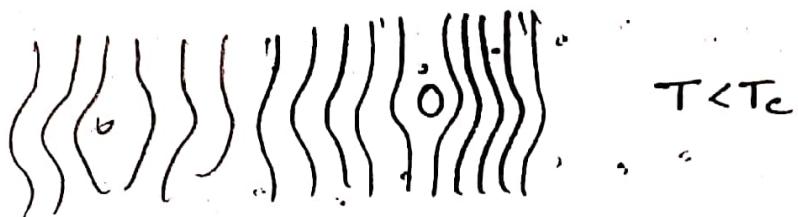
1. selectivity :- In SFE method we apply selected temperature and pressure
2. speed :- In SFE method speed depends upon diffusion of matrix and extracted materials

Limitations :-

In SFE method, we supply high pressure it increase the cost compared to conventional liquid extraction.

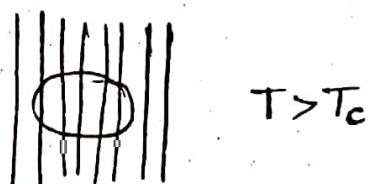
* Super critical fluid extraction method:-

In this method the extraction of food (coffee, sugar, polymers, petro chemi

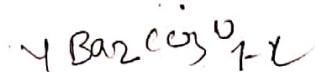
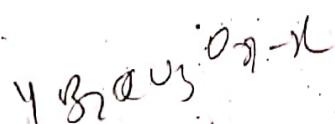


Type-II Superconductor (or) Hard superconductor:

- In this superconductor, it exhibits magnetisation, value is zero from lesser magnetic field to higher magnetic field.
- The critical temperature (T_c) is less when compared to normal temperature (T)



Example for superconductor:



Yttrium Barium Cuprate ($YBa_2Cu_3O_{7-x}$)

It contains yttrium oxide, barium carbonate, cuprous oxide in stoichiometric ratio (1:2:3) and hence is called 1:2:3 molar superconductor and $T_c = 90\text{K}$

Synthesis of 1:2:3 superconductor by ceramic method:

Step 1: Preparation of a homogenous mixture of three oxides (Y_2O_3 , $BaCO_3$ and CuO) in their molar ratios

Step 2: Heating them to obtain oxygen deficient superconductor in a muffle furnace.

Step 3: Annealing the above compound to room temperature to retain its composition, structure and superconducting properties

CLASSES OF SUPERCONDUCTORS:

- | | | |
|-----------------------|--|---|
| 1. Elements | Eg: Hg, Nb, La | E - Hg, La
Alloys - La ₃ In |
| 2. Alloys | Eg: La ₃ In, Nb ₃ Ge | simple com - NbN
molecular crystals - C ₆₀ X
ceram - mixed |
| 3. Simple compounds | Eg: NbN | Elem - tP, La/Nb (8)
Alloys - La/In |
| 4. Molecular Crystals | Eg: C ₆₀ K _x | sim - NbN
Mo - C ₆₀ K _x |
| 5. Ceramics | Eg: Mixed metal oxides | Ceramics - mixed metal oxides |
| 6. Inorganic Polymers | Eg: (SN) _x | In. - SN _x |
| 7. Organic compounds | | or - |

PROPERTIES OF SUPERCONDUCTORS:

- Sc are brittle, so used in preparation of electronic wires
- Thermoelectric property is zero
- The magnetisation property is zero
- When current is passed through the superconducting materials, the heating loss I^2R is zero.

APPLICATIONS OF SUPERCONDUCTORS:

- Used in MRI scanners
- $(YBa_2Cu_3O_{7-x})$ is used in industrial catalyst like hydrogenation, oxidation etc,
- Used as a alcohol sensor to prevent road accidents $(La_2Sr_xO_{3-x})$
- It is also used in preparation of electronic devices like cellular telephones.

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