Unit - II

Modern Engineering materials

In modern Engineering materials we will Explain about conductors, semiconductors, Insulators, super conductors, super capcitor and nano materials.

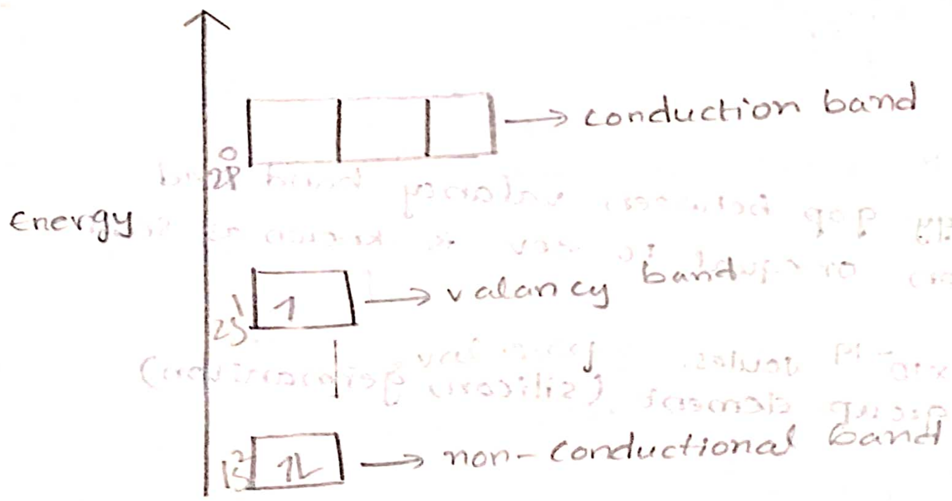
Band theory of solids :- (6M)

Flelix Bloch; proposed band theory of solids in 1926 to explain Band gaps of conductors, semiconductor and Insulators In periodic table We will take lithium element to Explain band formation in solid material.

The atomic number of 'Li' element is 3

The electronic configuration of 'Li' element is $1s^2 2s^1 2p^0$

Formation of bands in litium metal:-



Non-conductional band:-

1. The completely filled orbitals produce non-conduction band

2. In lithium metal is orbital produce non-conduction band.

3.

Valancy band:-

1. The paratially filled orbital produce valancy band.
2. In lithium 2s orbital produce valancy band.

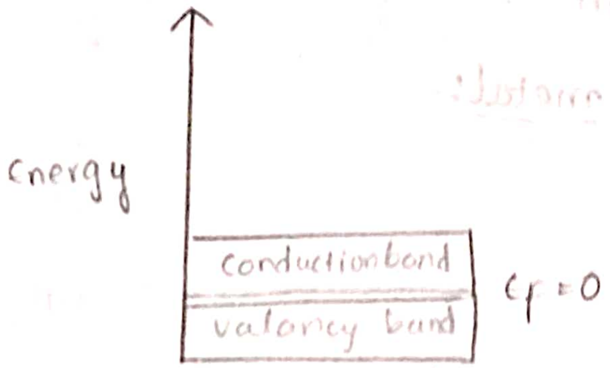
Conduction band:-

1. The empty orbitals produce conduction band
2. In lithium metal 2p orbital produce conduction band

Conductors:-

The fermi energy gap between valancy band and conduction band is zero i.e Both bands are overlapped. is known as conductors.

Eg:- All metals. Except mercury.

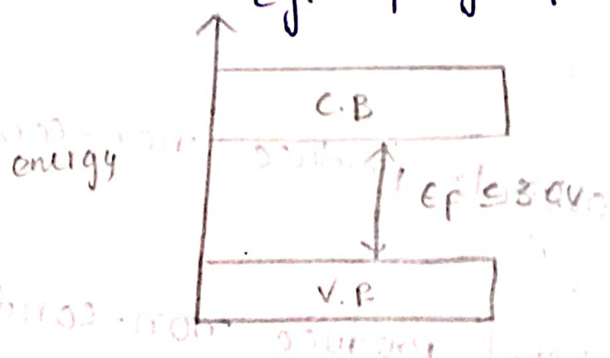


Semiconductors:-

The fermi energy gap between valancy band and conduction is less than or equal to 3ev is known as semi conductors.

Here, $1\ ev = 1.6 \times 10^{-19}$ Joules.

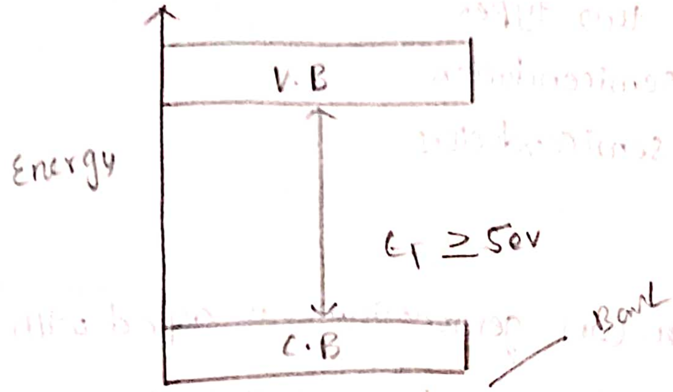
Eg:- 14^{th} group element (silicon, germanium)



Insulators :-

The fermi Energy gap between valany band and conduction band is greater than (or) equal to 5ev is known as Insulators

Eg:- wood, rubber, non-metals.



Classification of semi conductors:-

1. Intrinsic semiconductors:-

The another name of Intrinsic semiconductor is pure semi conductors

All the 14th group elements acts as Intrinsic semiconductors.

Eg:- Carbon, silicon, germanium, Scanum, lead etc.,

In Intrinsic semiconductors no. of electrons is always equals to no. of holes.

$$n_e = n_h$$

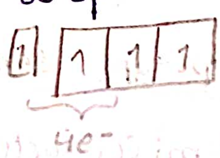
The atomic number of silicon is 14

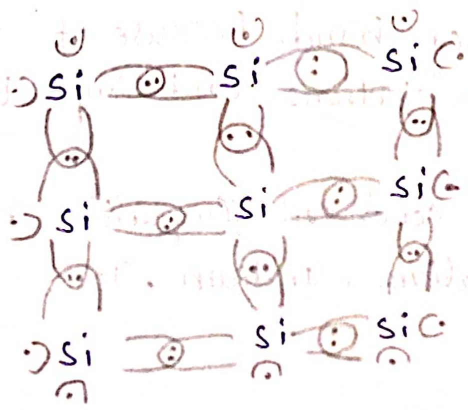
The ground state electronic configuration of silicon is

$$1s^2 2s^2 2p^6 3s^2 3p^2$$

The excited state configuration of silicon element is

$$1s^2 2s^2 2p^6 3s^1 3p^3$$





Extrinsic semiconductors:-

The another name of extrinsic semiconductor is Impurity Semiconductor.

on the based upon adding of Impurities extrinsic Semi conductors are divided into two types

a. p-Type semiconductors

b. n-Type semiconductors

a. p-Type semiconductor:-

The pure silicon (or) germanium is doped with 13th group elements as a Impurities to form p-Type semi-conductor.

Here,

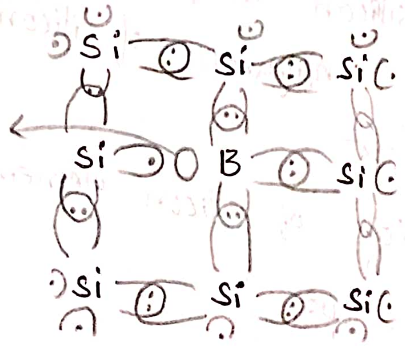
Impurities are trivalant because of which consist three valancy electrons.

In p-Type semiconductors majority charge carries are holes and minority charge carriers are electrons.

$$n_e <= n_h$$

B	Beta
Al	Alpha
Ga	gama
In	In
Tr	Triangle

holes

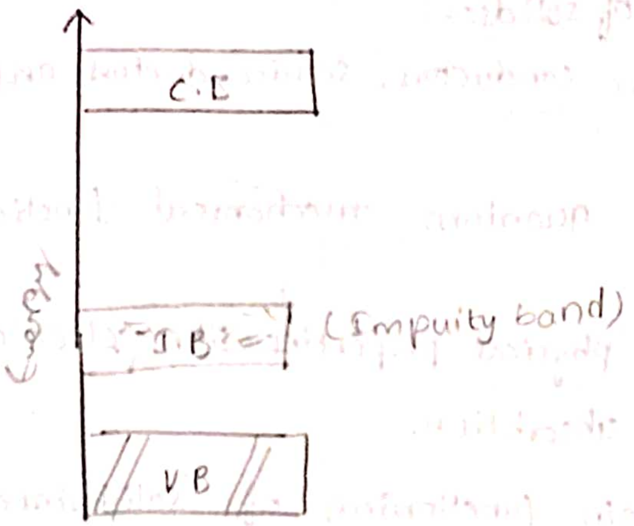


holes having lesser mobility than that of electrons

Effect of doping in p-type semiconductor:-

In p-Type Semi Conductor Impuritie band is closely attached to the valancy band. because of attraction forces between valancy band electrons and impuritie band holes

In p-type Semi Conductors Impuritie materials are Boron, Aluminium, Galium, Indium, Tr

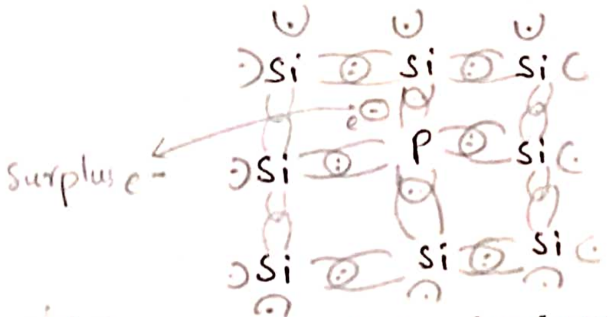


n-type semiconductors.

The pure silicon (or) germanium attached with 15th group elements as a Impurities to form n-type semi conductors. Here, Impurities having five valancy electrons so, name of the Impuritie is pentavant Impurity.

In n-Type semiconductor electrons are majority charge carriers. holes are minority charge carriers.

$n_e > n_h$

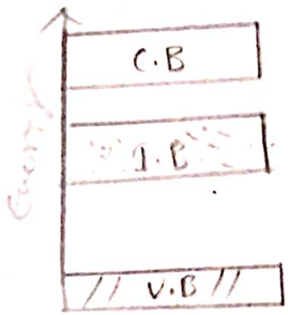


electrons are free (or) carriers and are present in conduction band electrical conductivity depends upon mobility of charge carriers

effect of doping in n-type semiconductor:-

In n-type semiconductor Impurity band is closely attached to the conduction band because of attraction fore between conduction band empty region and Impurity band surplus electrons.

In entire Semiconductor our Impurities are Nitrogen, Phosphorus, Arsenic, stibium, Bismuth.



Applications of Band theory of solids:-

1. It is used to explain conductors, semiconductors and Insulators.
2. It is used to explain quantum mechanical functional Values.
3. It is used to explain physical properties like electrical Resistivity and optical absorbtion.
4. It is used to explain functioning of solid state devices like Transitors and solar cells.

fermi level:- (P.M)

It is the highest energy state occupied by free electrons at absoulte zero Temperature.

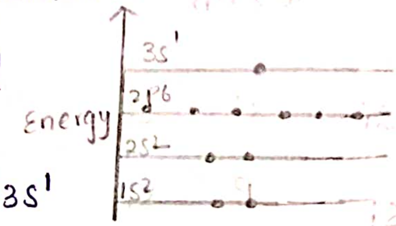
fermi Energy:- (Richardson)

It is the maximum energy possesed by free electrons at absolute zero Temperature.

Example :- Sodium Metal

$Na\ (z) = 11$

$E.C = 1s^2 2s^2 2p^6 3s^1$



Super conductors:-

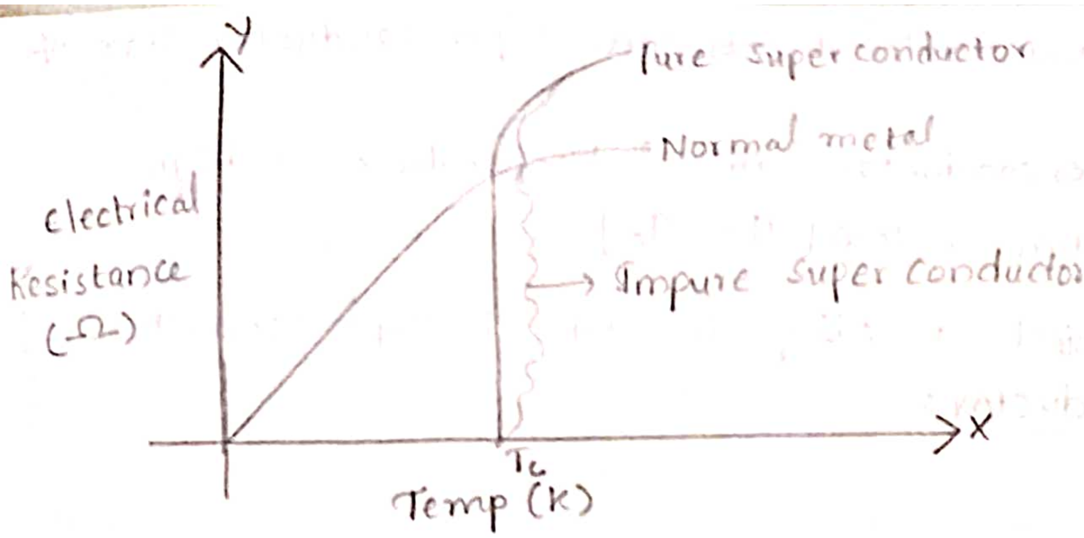
A Dutch physicist Kommer lingh onnes proposed Super conductors. in 1911.

Definition:-

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

* Super conductors explain by the following graphical representation.

Imp Conductors difference Super conductor.



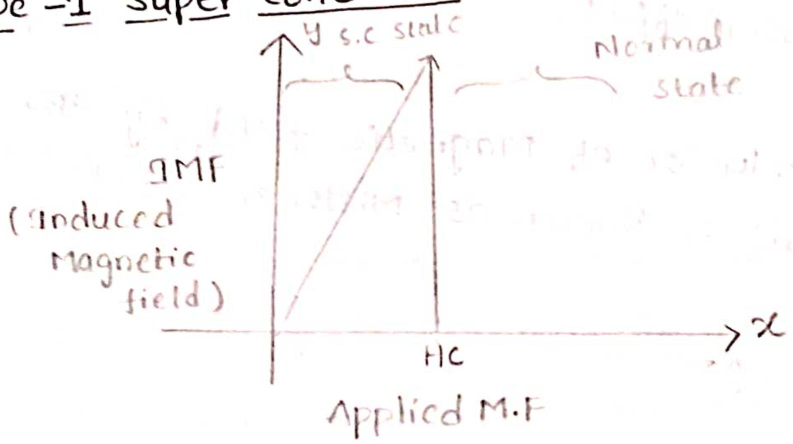
Critical Temperature (T_c):-
At which Temperature the material converts from super conducting state to normal state is known as critical temperature. (electrical resistivity drops to zero)

* Below the critical temperature the material acts as super conducting state.
* Above the critical temperature the material acts as Normal state Eg:- Aluminium - 1.2K, Indium :- 3.4K, Mercury 4.2K, Lead 7.2K

Classification of superconductors:-
On the based upon character of superconductors these are divided into two types.

1. Type - I (or) soft super conductors
2. Type - II (or) Hard super conductors

Type -I super conductors :- (7 points difference)



1st point name
2nd graph
3rd How many Magnetic fields
4. critical Temp
5. Misner Effect
6. below Hc
7. Misner effect case (i) & case (ii)

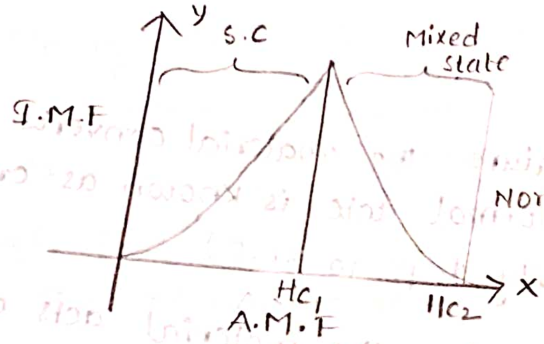
In Type - I Super conductors We have only one critical Magnetic field point (Hc)

* Below the Hc that material acts as super conductor state of Metal.

* In Type-I superconductor critical temperature is high normal temperature is low [$T < T_c$]

* The Miessner effect is obeys in Type-I super conductors.

<u>Type-II Super conductor</u>:-



In Type-II super conductor We have two critical Magnetic field point those are H_{c_1} and H_{c_2}.

* Below the H_{c_1} that material acts as a super conducting state.

* In between H_{c_1} and H_{c_2} that material acts as a Mixed state.

* Above the H_{c_2} that Material acts as a Normal state.

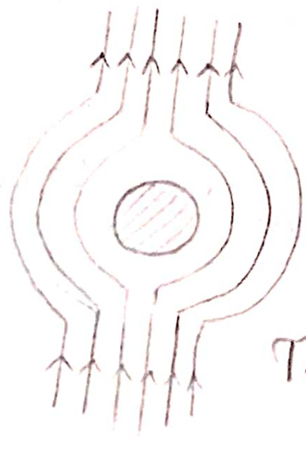
* In Type-II super conductor critical temperature is low, normal temperature is high. [$T > T_c$]

* It does not obeys Miesser effect.

<u>Miessner effect</u>:-

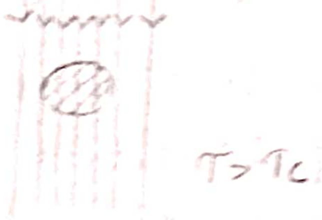
The complete exclusion of Magnetic field by the Super conductivity materials is known as Miessner effect.

<u>Case (i)</u>: $T < T_c$



$T < T_c$

Case (ii): $T > T_c$



Properties of super conductors :-

* The super conductors having brittle nature that means which forms very thin layer sheets.
* The super conductor material exhibits copper loss equation is zero (0) ($I^2R = 0$) that means input current is equal to output current.
* The super conductors material shows strong magnetic field. that means strong attractions and repulsion forces in magnetic field.
* Miesser Effect :-
  The complete explosion of magnetic field by the super conducting material is known as Miesser Effect.
  → Type-I super conductor exhibits Miesser Effect.
* The super conductor materials exhibits dia-magnetic nature.
* The super conductor materials shows Thermo electric effect is 'zero' that means the continuous usage of electrical component which produce heat energy.

Applications :-

* Generally silicon chips are used storage devices we replace with super conductor chips these are 100 times better than the traditional silicon chips.
* The super conductors materials are used to manufacturing of MRI scanning (Magnetic Resonance Image)
* The super conductor materials are used to find out alcohol content present in body ($La_{2-x} Sr_x Cu_8 O_7 - x$) with the help of $K_2Cr_2O_7$ substance.

* Super conductors Materials are used as Industrial Catalyst to speed up Dehydro halogination reaction.

* The Super Conductor Materials is used to prepare Maglev trains in the presence of Levitation effect [The attraction force between super conductor Material and earth gravitation forces). [Speed capacity 500 km/h]

Super capacitors:-

Layman Example:-

⇒ In 200m Running race we require large amount of energy to reach destination. This character is Super Capacitors.

⇒ In 20km running race we require small amount of energy to reach destination. This character is known as Battery.

Becker proposed super capacitor in 1957 which are used in electrical buses in shangai, china

Definition:-

The material which is stored maximum amount of electrical energy compared to battery known as super capacitors.

Construction of super capacitor:-

In the construction of super capacitor require two equal length of plates which as anode and cathode. Both are connected the help of semipermable membrane ~~keep~~ and electrolyte substance.

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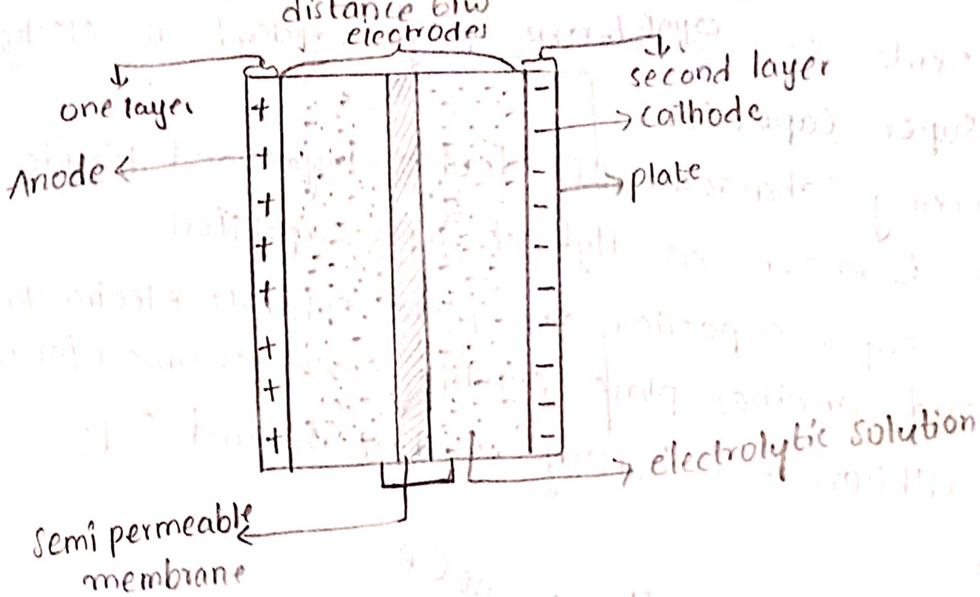


Principle :-

$$C = \frac{\varepsilon l}{d}$$

where C = capacitance
ε = dielectric constant
l = length of the plate
d = distance b/w electrodes

Dielectric constant (ε) :- (2M)

In super capacitor anode plate attracts negative charge ion to form one layer. cathode plate attracts positively charge ions to form another layer. Both layers produce some electrode potentials is known as Dielectric constant. (ε)

Classification :-

on the based upon attraction forces super capacitors are divided into three types.

1. **Double layer super capacitor** :-

In this super capacitor exhibits electrostatic attraction forces between the electrodes

* Carbon electrodes (or) Allotropy of carbon elements (cnts, Graphene) acts as electrodes.

2. **Pseudo super capacitor** :-

In this super capacitor behave electrochemical attraction forces between the electrodes and electrolyte solution.

* Metal oxides (or) conducting polymers acts as electrodes.

3) Hybrid Super Capacitor:-

The mixing character of double layer and pseudo capacitors is known as Hybrid super capacitors.

In this super capacitor one plate exhibits electrostatic forces and another plate exhibit electro chemical forces.

The lithium ion battery used as hybrid super capacitor.

Properties of Super Capacitors:- SHEL²R

1. long life
2. High storage
3. Low cost
4. stablizing
5. Rapid charging.
6. Energy Releasing.

Applications:-

1. Super capacitors used in laptop computers.
2. Electrical vehicles
3. Laser Medical Equipment
4. Industrial catalyst
5. electronic digital switching devices.

Nano Chemistry:-

It is a branch of chemistry which deals preperations, properties and applications of nano materials.

1 nanometers $= 10^{-9}m =$ 1 billionth of meter.

Nano materials:-

The material which exhibits at least one dimension between 1nm to 100nm (1nm - 100nm) is known as Nano materials.

Classification:-

1. Nano layer:-
The Nano material which exhibits one Dimension between 1nm – 100nm is known as nano layer.

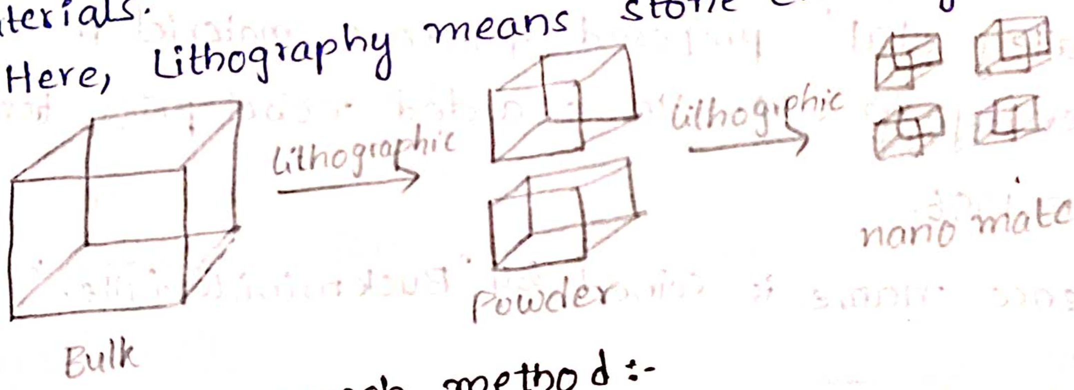
2. nano tube:-
The nanomaterial which Exhibits Two dimensions between 1nm – 100nm is Known as nano tube.

3. Nano particle:-
The nano material which exhibits Three dimensions between 1nm - 100nm is known as nano particle.

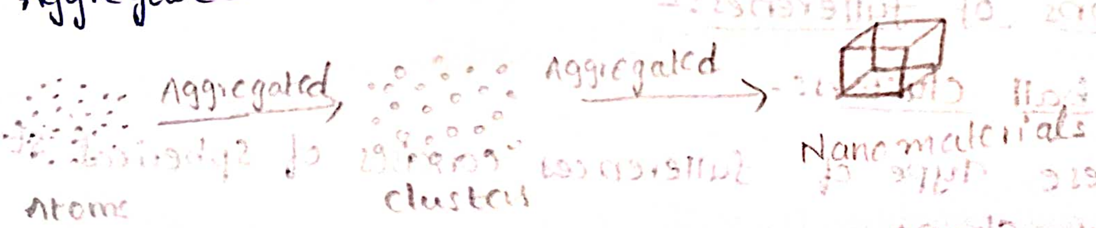
4. Quantum Dot:-
The semiconductor material which exhibits one dimensions between 1nm– 100nm is known as "Quantum dot"

General methods for preperation of nano materials

1. Top–down approach method:-
The bulk material undergoes Lithographic method to form powder. powder undergoes lithographic method to form nano materials.
→ Here, Lithography means stone crushing technique



2. Bottom-up approach method:-
Atoms are Aggregated to form clusters, Clusters aggregated to form nano materials.
→ Here, Aggregated means Collection.



Properties of nanomaterials:- MCTSM H'TCS
Based upon size :-
1. Magnetic behaviour - diamagnetic nature

2. Colour - Gold is in bulk gives yellow colour in nano size it is red colour.

3. Transperency - Object visiblity character.

4. Solubility - Sparingly soluble in organic solvents.

5. Melting point - low Melting Point.

Based upon composition :- C'R

1. collidal :- This nature of nano materials is known as coercing collidal.

2. chemical Reactivity - Normal.

3. Reaction rate - Normal.

Base upon surface :- C^2D

1. Conductivity - Semiconductor property
2. Dispersibility - seperation
3. catalytic - To speed up the reaction.

Fullerenes :-

"Richard Smalley otal" proposed fullerens material in 1985 at Rice university in USA. He awarded nobel prize for this concept in 1996.

→ The fullerence name is coined by "Buckminister fuller"

Definition :-

It is an allotrophy of carbon element which have ellipse, tube, spherical structure is known as fullerence.

Classifications of fullerenes :-

1. Bucky ball clusters :-

These Type of fullerences consists of spherical strcutures in ball shape.

ex :- C_{20} and C_{60}

2. Carbon nano Tubes (CNT's)

This Type of fullenes having hallow tube structures with small dimensions.

Ex:- SWCNT's, MWCNT's (single wall & Multi wall)

3. Megatubes:-

The fullerence which consiting of large dimensions is known as Mego tubes.

4. Polymer:-

The two dimensional and three dimension polymer materials. under goes HighTemperature and High pressure to form fullerene nano Materials.

5. Boron Bucky balls:-

The carbon Element is replaced with Boron to form Boron Bucky balls.

Ex:- B60 and B80

6. Nano onions:-

The fulleren materials which having multiple layers in its structure like onions is known as nano onions.

7. linked ball and chain dimers:-

The Two (or) more bucky ball clusters attached in chain wise manner to form linked ball and chain dimers.

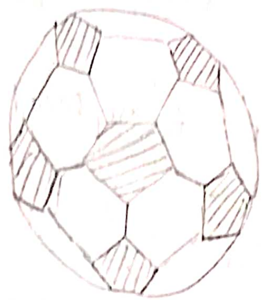
8. Metallo fullerence:

The fullerene which consist of 80 carbon elements, 3 Metal atoms and one Nitrogen atom to form Metallo fullerence.

Imp fullerene carbon nanotubes difference

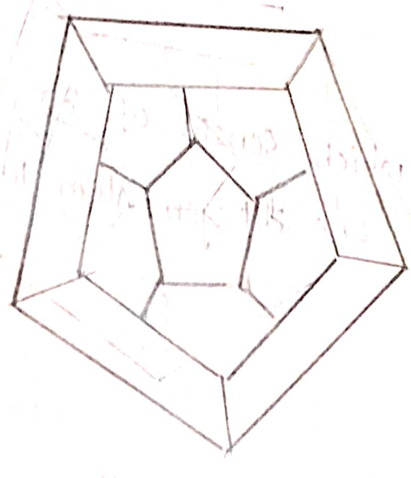
C_{60} fullerene (Buckminister fullerene)

1. The Iupac name of C_{60} fullerene is "Truncated icosahedra"
2. In this fullerene carbon element undergoes sp^2 hybridisation.
3. In this fullerene having Twelve pentagonal and Twenty hexagonal rings.
4. The shape of the fullerene is Soccer ball.
5. The bond length of the fullerene is 1.4 A°
6. The Bond diameter of fullerene is 1.1 nm



C_{20} fullerene :-

1. It is a smallest fullerene
2. The Iupac name of fullerene is "unsaturated dudecahedrane"
3. In this fullerene carbon element undergoes sp^2 Hybridisation



Properties of fullerene:-

1. Endo hedral fullerence means Inclusion forces we get the egg shaped fullerene
2. chirality → different functional valency.
3. Sculpturing → designing of ceramics
4. Addition of oxygens → epoxides → C600
5. Addition of halogen → halogenated fullerene → $C_{60}Br_8$ (or) $C_{60}B$
6. Addition of hydrogens → Polyhydro fullerene
7. Solubility → Sparingly soluble → CS_2 (or) Toulene

Applications:-

1. used as Hydrogen fuel
2. It is used as Solar cells (or) solarpanels
3. used to Inhibit HIV Virus.

Applications of Nano materials:-

1. electronic digital switching devices
2. Solar cells and Semi conductors
3. Agricultural and genetic Improvement
4. Biomedical Applications.
5. Mechanical.

Carbon nano Tubes:- (CNT's)

Sumio Iijima proposed carbon nano tube in 1991. He was Japanese physist.

Definition:-

It is an allotrophy of carbon element having graphite sheets of hegonal ring layers above 0.4nm as a diameter.

Classifications :- SMTN²PGC

1. Single wall Carbon nano tubes (SWCNT's)

The carbon nano tubes which consisting of mono layer of hexagonal rings is known as SWCNT's.

2. Multi wall carbon nano tubes (MWCNT's)

The Carbon nano tubes which consisting of two (or) more hexagonal rings is known as MWCNT's

Eg:- A) Russian doll model — No edges.

B) Pechmend model — edges.

3. Torus (-Toarus) 

The donut shape of carbonnano tubes is known as Taurus. doughnut

4. Nano bud:-

The CNT's are attached with fullerence either Top side (or) Bottom side is known as nano bub.

5. N- doped CNT's:-

The CNT's are attached with 15th group elements (Nitrogen family) as a Impurities. to form n- doped CNT's

6. Pea pod :-

The fullerences are attached inside of the CNT's like Peanut manner is known as pea pod CNT's

7. Graphenated CNT's:-

The CNT's are attached with Graphene nano Particles and graphite materials. to form graphinated CNT's

8. cup stacked:-

The CNT's are arranged in cup stacked manner is known as cup stacked CNT's

Properties :-

1. strength → 100 GPa
2. Hardness → 25 GPa
3. electrical → conducting
4. electro magnetic wave absorbtion → Military radars.
5. optical → Raman spectro scopy
6. Thermal stability → Cu - 385 $wm^{-1}k^{-1}$, CNT's - 3500 $wm^{-1}k^{-1}$
7. Toxicity → Inflammetary and fibrotics
8. kinetics → Telescope's. (Anti striking Telescopic Property)

Applications of carbon nanotubes :-

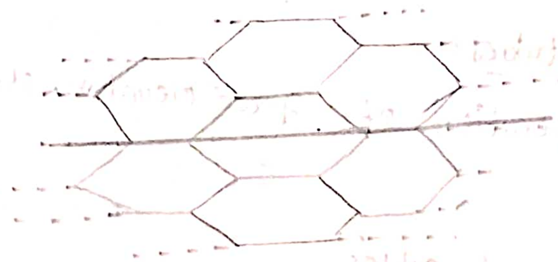
1. CNT's are used in preperation of space elevators, stabproof and Bullet proof materials.
2. These are used in electrical cable's
3. Paper battery's :- In this battery's CNT's acts as electrodes, cellulose derivatives (green wood material) acts as electrolyt
4. Textile Industry :- The CNT's are used in manufacturing of Anti-bacterial fabrics
5. food stoorage containers.
6. Medical fields. The CNT's are used to inhibit tumerous ~~tumors~~ cells (or) cancers cells.
7. solaor cells, Hydrogen fuel.

Graphene Nano particles :-

→ Andrewgain and Konstauline novosdove proposed Graphane Nano particles in 2003. by the cleaning of wastage graphite. They awarded noble prize in 2010

Definition :-

It is an allotropy of carbon elements having unbreakable structures hexagonal ring layers with honey comb lattice is known as Graphene Nano particles.



Graphene nano particles are zero band gap conductor because valancy band and conduction band connected at specific center (or) ~~de~~ specific line is known as dirac point (or) dirac center

Preperations :-

1. Top-down approach method

a) Mechanical Exfoliation :-

In this method we apply mechanical Energy like compression, pressure and temperature to form graphene nano particles

→ our scientist prepared graphene nano particle by mechanical Exfoliation method.

b) Chemical Exfoliation :-

In this method carbon material Interacts with alkali metal (H, Li, Na, K, Rb, Cs, Fr) to form graphene nano particles.

Helinaki rubina class frind

2. Bottom-up approach method:

a) Chemical vapour deposition :- (CVD)

In this method gaseous state of carbon material Interacts with Nickel (Ni) metal as a substate to form graphene nano particles in the presence of cooling phase

b) Atomic layer deposition:-

It is one of the type of chemical vapour deposition methon.

Properties:- S^2 T 3HLY

1. Strongest Material
2. Thinest material
3. Young's modulus is zero $\frac{stress}{strain} = 0$
4. Transmission is 98 %.
5. High conductivity.
6. Semi conductor
7. little scattering
8. Transperancy (visibility)

Applications:-

1. Integrated Circuits & Transistors
2. desalination. (reverse osmosis) (h.c - L.c)

The process of removal of salt from the sea water is known as desalination. In desalination process we use graphene nano particles as a semipermeable membrane.

3. gas sensors:-

Graphene nano particles are used to Identify pollution gases present in Environment

4. Solar cells:-

The graphene nano particles used as Solar panles which Produce maximum amount of electrical Energy when compared to traditional silver panles.

5. flexible mobiles :- (foldable character like paper)