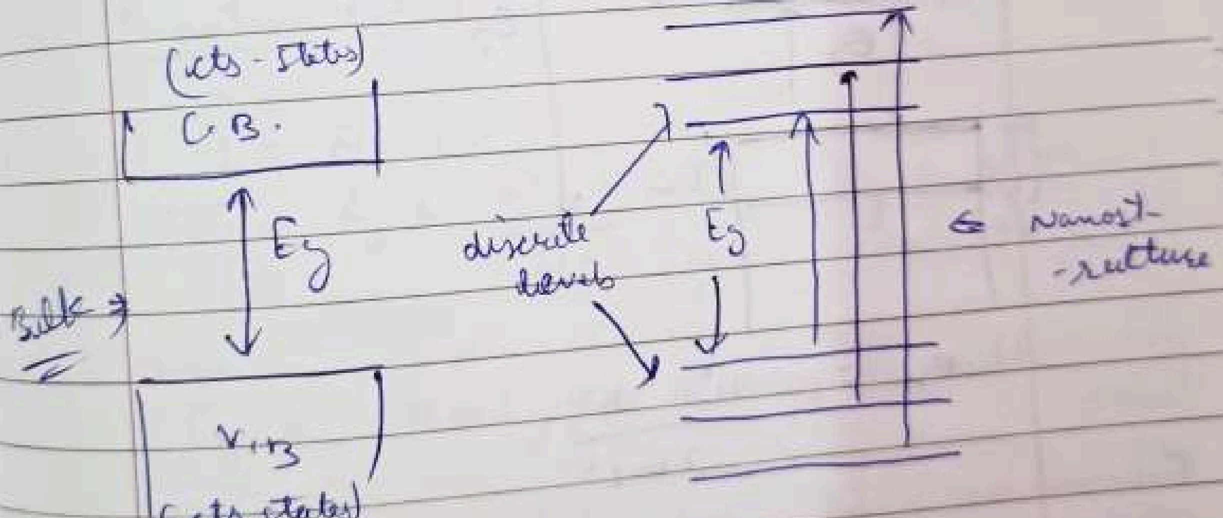
① Quantum confinement :-

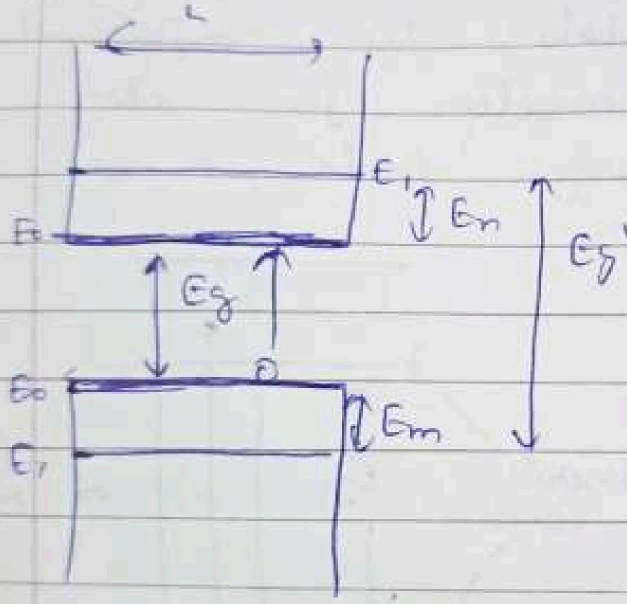
In nanomaterials, the electronic energy levels are not cts as in bulk but are discrete, because of confinement of electronic wave fun to physical dimensions of particles. This phenomena is called Q.C & ∴ nanocrystals are referred to as quantum dots. The confinement leads to a transition from cts to discrete energy levels.



A quantum confined structure is one in which motion of $e^{\ominus}$ & holes are confined in one or more dir by pot. barrier.

When materials are so small that they lie in Q.C regime, then their electronic & optical prop. deviate substantially from those of bulk materials. The discrete structure of energy states leads to a discrete absorption spectrum of nanostructure

ie. Bulk → nanoscale
↓
cts → discrete



$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

$$\therefore E_g' = E_g + E_n + E_m$$

$$E_g' = E_g + \frac{n^2\pi^2\hbar^2}{2m_eL^2} + \frac{m^2\pi^2\hbar^2}{2m_hL^2}$$

if $n = m = 1$

$$E_g' = E_g + \frac{\hbar^2\pi^2}{2m_eL^2} + \frac{\hbar^2\pi^2}{2m_hL^2}$$

$$E_g' = E_g + \frac{\hbar^2\pi^2}{2L^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right)$$

$$= E_g + \frac{\hbar^2\pi^2}{2L^2}\left(\frac{m_h + m_e}{m_e m_h}\right)$$

$$\because \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$ reduced mass

$$\boxed{E_g' = E_g + \frac{\hbar^2\pi^2}{2L^2\mu}}$$

Quantum dot.

$$L = D = 2R$$

$$E_g' = E_g + \frac{\hbar^2\pi^2}{2(2R)^2\mu} = E_g + \frac{\hbar^2\pi^2}{8R^2\mu}$$

where

E_g = Band gap energy of Bulk

$\frac{\hbar^2\pi^2}{8R^2\mu}$ = energy due to confinement

Optical transitions in Q.D. are usually associated with excitons & an approx expression given by Brus eqⁿ model in which transition energy in spherical dots

Brus eqⁿ

$$E_g^{dot} = E_g + \frac{\hbar^2\pi^2}{8R^2\mu} - \underbrace{\frac{1.8\,q e^2}{4\pi\epsilon_0\epsilon_r R}}_{\text{B.E. of exciton}}$$

Bohr model

$$\frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2} = \frac{mv^2}{r}$$

$$v^2 = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2}\cdot\frac{r}{m}$$

$$v = \sqrt{\frac{1}{4\pi\epsilon_0}\frac{e^2}{mr}} = \sqrt{\frac{Ke^2}{mr}}$$

$$\because \quad mvr = n\hbar$$

$$m\sqrt{\frac{Ke^2}{mr}}\cdot r = n\hbar$$

$$\sqrt{\frac{Ke^2}{mr}} = \frac{n\hbar}{mr}, \quad \frac{Ke^2}{mr} = \frac{n^2\hbar^2}{m^2r^2}$$

$$r = \frac{n^2\hbar^2}{m^2Ke^2}$$

S.B.S.

$$\boxed{r = \frac{n^2\hbar^2}{Ke^2m}}$$

$$n=1, \quad a_0 = \frac{\hbar^2}{Ke^2m} = \frac{4\pi\epsilon_0\hbar^2}{e^2m_e}$$

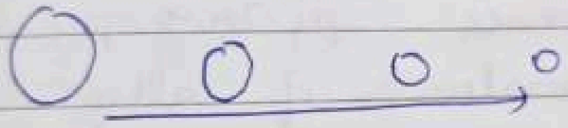
$$a_{ex} = \frac{4\pi\epsilon_0 \epsilon_r \hbar^2}{e^2 \mu} \times \frac{m_e}{m_e}$$

$$a_{ex} = \frac{a_0 \epsilon_r m_e}{\mu} = \frac{(0.53)\, \epsilon_r m_e}{\mu}$$

i) Spherical dot ($R >> a_{ex}$)

Q.C effect doesn't occur

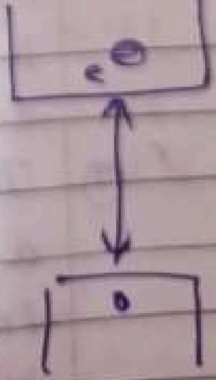
ii) if $R > a_{ex}$ ⇒ weak Q.C effect arises



i.e. $E_{g_1} < E_{g_2} < E_{g_3} < E_{g_4}$

(iii) if $R < a_{ex}$ ⇒ strong Q.C effect occur

$$E_g^{dot} = E_g + \frac{\hbar^2 \pi^2}{8\mu R^2} - \frac{1.8\, e^2}{4\pi\epsilon_0\epsilon_r R}$$



$$E_g^{dot} = E_g + \frac{\hbar^2 \pi^2}{8\mu R^2}$$

$$\boxed{E_g^{dot} - E_g = \frac{\hbar^2 \pi^2}{8\mu R^2}}$$

Unit - 4

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U-4

① Discuss increase in width of XRD peaks of nanomaterials.

② Discuss how you can find the size of nanomaterials.

③ Discuss variation of Raman spectra in case of nanomaterials.

④ Discuss shift in photoluminescence peaks in case of nanomaterials.

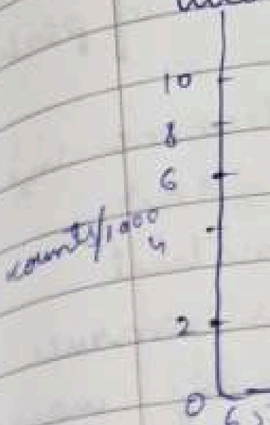
⑤ Describe the basic principal & instrumentation involved in photoluminescence spectroscopy. Discuss how photoluminesence spectroscopy is used in determination of alloy composition in compound semiconductors ($Al_xGa_{1-x}As$) etc & in finding the well width of $Al_xGa_{1-x}As/GaAs/Al_xGa_{1-x}As$ quantum well structure.

⑥ How to distinguish b/w bulk & nano-crystalline materials using X-ray diffraction technique? Derive a relationship that incorporates the effect of both finite size of nano particles & strain on broadening of X-diffraction peaks.

⑦ The photoluminesence (PL) spectrum of a sample of four quantum wells (a, b, c, & d) of diffⁿ width shown below, arrange the wells in ↑ing

order

with



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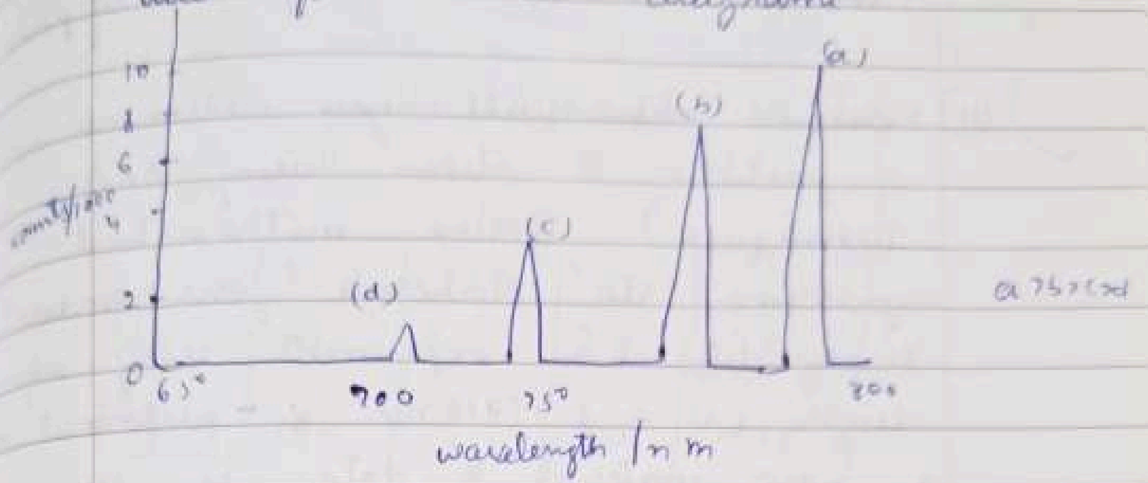
order of width & justify your ans with formulas & diagrams



⑧ Explain the basic principle of Raman & Photoluminescence spectroscopy. Discuss the effect of particle size on broadening of Raman peaks.

⑨ X-ray diffraction expt using $\lambda = 0.15418$ nm is performed on a nano-materials & data is summarized in table. Using this table determine the average particle / crystallite size.

Peak	$2\theta(°)$	$\cos\theta$	hkl	FWHM $\beta(°)$
1	38	0.9455	111	0.187
2	44	0.9272	200	0.206
3	66	0.8387	220	0.271

4 ⑩ Discuss how inhomogenous strain leads to broadening of X-ray

diffraction peaks while homogenous strain changes the position of peaks.

(11) Discuss how will you determine size of particles & strain using XRD techniques? Derive mathematical expressions to elaborate your. answer. X-ray diffraction experiment using wave-length (λ) = 0.15418 nm is performed on a nano material & data is summarising in table. using this data determine the avg particle / crystallite size

Peak	2θ(°)	Cos θ	hkl	FWHM β(°)
1.	38	0.9455	111	0.187
2	44	0.9272	200	0.206
3.	66	0.8387	220	0.271

(12) explain Raman effect? Discuss the effect of particle size on broadening of Raman peaks;

(13) Describe principle of photoluminescence spectroscopy (PL). How it is employed for characterization of nano-materials

(14) explain with neat & clean dia. That uniform strain leads to shifting of X-ray peaks while non-uniform strain causes peak broadening.

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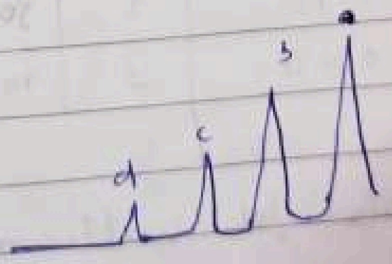
⑮ A cubic crystal was placed in an x-ray diffractometer using incoming x-ray with a $\lambda = 0.154$ nm. The various peaks intensities recorded at diffⁿ 2θ values &

2θ	40.3	58.3	73.2	131.2
hkl	110	200	211	321
Relative intensity	100	15	23	18

calculate particle / crystallite size & lattice parameter (a). You are provided with $k = 0.91$ & FWHM (β) of max intensity peak = 0.56 degree.

⑯ The PL spectrum of a sample of 4 quantum wells (a, b, c, d) of diffⁿ width is shown below: arrange the wells in Incr. order of width & justify your ans with mathematical expression & figure.



(i) ⑰ explain various sources of line broadening of XRD peaks of nano-materials & S.T. (i) in nano-materials without micro-strain, the FWHM due to

(2)

finite size of crystallites is given as

$$\beta_c = \frac{K\lambda}{\cos(\theta_B)\, L}$$

K = scherrer const ; L = avg crystallite size

(ii) micro strain leads to broadening of XRD peaks & its contribution is given as

$$\beta_{strain} = \eta \tan(\theta_B)$$

⑦ X-ray diff. data of a heavily cold-rolled copper powder & a well annealed copper powder is presented below

X-ray radiation : Cu kα , λ = 0.154056 nm

Peak profile : Gaussian

Annealed Cu				Cold rolled Cu			
Peak	2θ(°)	hkl	FWHM(°)	Peak	2θ(°)	hkl	FWHM
1	43.16	111	0.260	1	43.31	111	0.465
2	50.30	200	0.330	2	50.40	200	0.541
3	73.55	220	0.438	3	74.19	220	0.676

Prepare data for williamson - Hall's Plot & fit using least square method to find the avg crystallite size & lattice strain in cold rolled Cu powder.

imp ② =)

Determination of Particle Size

Particle size determination is a collective name of techniqual procedure which determine the size, range or mean size of the particle. The particle's size can have importance in no. of industry including the chemical mining, forests, agriculture & industries. There are various methods of particle size determination :-

(a) XRD :- X-ray diffraction is very imp experimental technique that has been used in determine the grain size. The grain size is determined by the broadening of XRD peak. This peak broadening is normally caused by finite size of crystal. If the average size of crystal is below 200 nm then broadening of XRD occur. The grain size can be calculated by formula given by Debye Scherer

i.e.- $D = \frac{k\lambda}{\beta\cos\theta}$

k = debye's const (0.9) , λ = wavelength of XR (about 1Å)

Date

θ = angle of diffraction
β = FWHM of given signal

X-ray peak is desired from the sum of different peak generated from different atoms.

As nano particles have much less atoms. Hence, the lattice sum is not able to ~~a~~ broadened.

The smaller the particle, the broader will be the diffraction peak. Broadening can be used to measure the size of the particle.

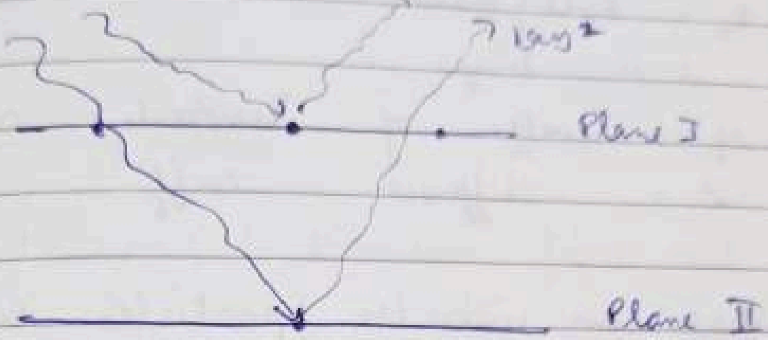
On the either side of Bragg's angle, the diffracted beam will interfere destructively & results in sharp peak. The destructive interference is a result of summation of all diffracted peaks. the Debye Scherer formula can also be written as

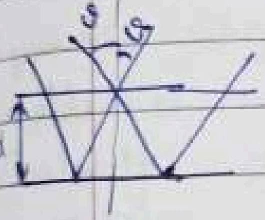
$$D = \frac{K\lambda}{(\beta_s - \beta_c)^{1/2} \cos\theta}$$

β_s = FWHM of standard sample
β_c = " " calculated "

In XRD, X-rays interact with ele$^{\ominus}$ &

transmit it's energy to $e^{\ominus}$ so that $e^{\ominus}$ begin to vibrate as $e^{\ominus}$ come to rest it emits radiations in other dir^{n}





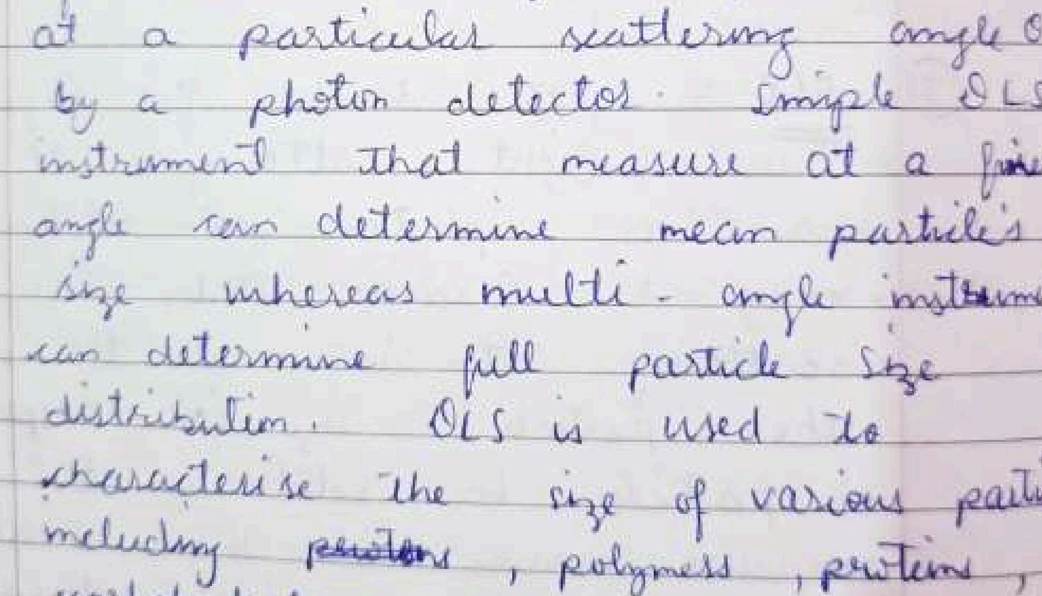
For constructive
$2d\sin\theta = n\lambda$

② <u>DLS</u> :- It stands for dynamic light scattering. It is also known as photon co-relation spectroscopy & Quasi-static light scattering. It is used to determine the particle's size in suspension of particles in solution. DLS can measure nano volt size. Smaller particles in suspension undergoes random thermal motion known as Brownian motion. The diameter of particle can be determine by Stoke's einstein relation

$$D_m = \frac{k_B T}{3\pi\eta D}$$

k_B = Boltzmann's const
t = temp
η = coeff. of viscocity
D = diffusion coeff.

DLS can measure particle's size upto 1nm in diameter. The basic principle is simple. The sample is illuminated by laser beam & fluctuation of scattered light are detected at a particular scattering angle θ by a photon detector. Simple DLS instrument that measure at a fixed angle can determine mean particle's size whereas multi-angle instrument can determine full particle size distribution. DLS is used to characterise the size of various particle including , polymers, proteins, carbohydrate & nanoparticles.



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The measurement of particle's size depends upon size of particle core, size of surface structure, particle conc & types of ions in the medium

③ Raman Effect

In 1928, CV Raman find out that when beam of light is passed through a transparent substance, a small amount of radiation energy is scattered. If a parallel beam of monochromatic light of frequency ν_c is incident on a given sample which doesn't absorb this light. The scattered energy will consists of same freq. radiation called as Rayleigh scattering. In addition to the incident freq. certain discrete freq. above or below of incident radiation will be scattered. This is called as Raman scattering. The Raman lines appearing at freq. lower than the freq. of incident light is called as stokes line, whereas line observing at freq. higher than the freq. of incident light is called anti- stokes lines.

Variation of Raman Spectra of molecules

When an incident photon interact with a chemical bond, the chemical bond is excited to higher energy state. Most of the ~~E~~ energy would be re-radiated at same freq. as that of incident light which is known as Rayleigh scattering. A small portion of energy is Transferred & results in excitation modes & This raman process is called as stoke scattering. (When the subsequent reradiated with a freq. lower than the freq. of incident light)

If the particle or atom already present in exciting state, then incident photon interact with these & gives an increase in reradiated energy. This is termed as anti- stoke lines.

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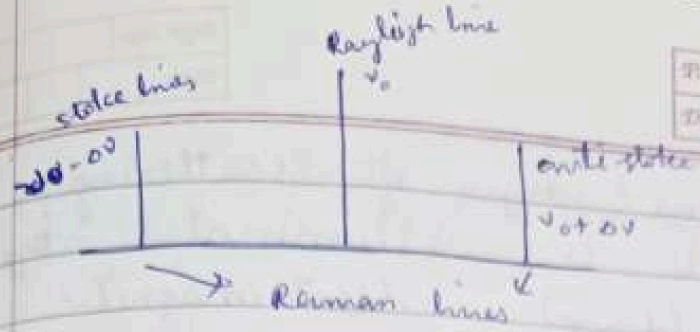


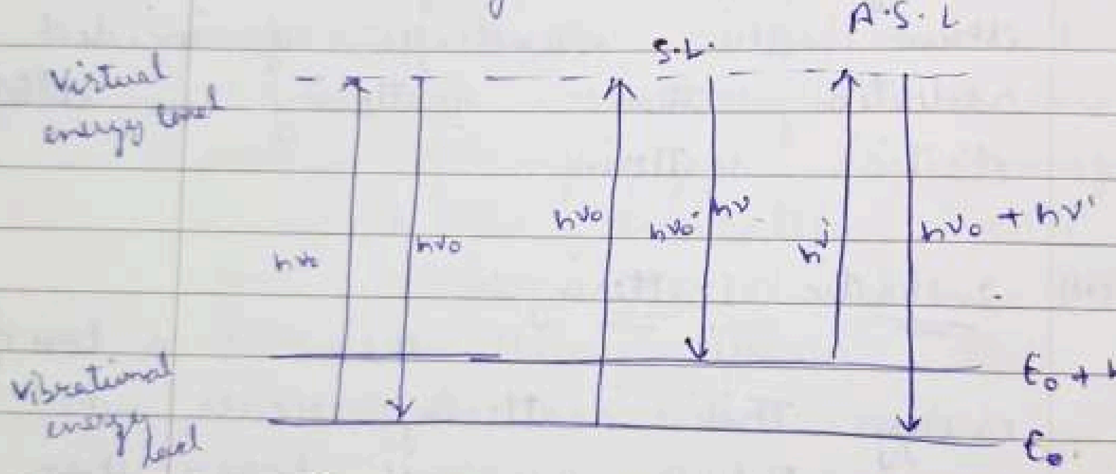
Raman scattering is also called as Photon scattering There are two types of photon scattering:-

(I) Elastic scattering:- there is no loss of energy when the particles dimensions are of the order of or smaller than the wavelength of incident radiation then scattering is called elastic scattering.

(II) Inelastic Scattering:- there is a loss of energy. This scattering occurs when the particle size is larger than the wavelength of incident radiation This type of scattering is known as Raman Scattering. Raman scattering is also called as Resonance Raman spectroscopy.

Raman Shift:- It is observed in terms of wave no. $\bar{\nu}$ which has unit equals to reciprocal to the units of wavelength $\bar{\nu}\,(cm^{-1}) = \frac{1}{\lambda_{inc}}$

In this type of scattering, a sample is illuminated by laser beam (lamp). Electromagnetic radiation from illuminated spot is collected with a lens & send through a monochromator. Elastic scattered radiation at wavelength closer to the wavelength of incident light are filtered out whereas the other radiation of different wavelength are detected by detector.



Energy level dia. showing transition b/w virtual & vibrational energy level.

A from above dia., there are three different pble. outcomes:

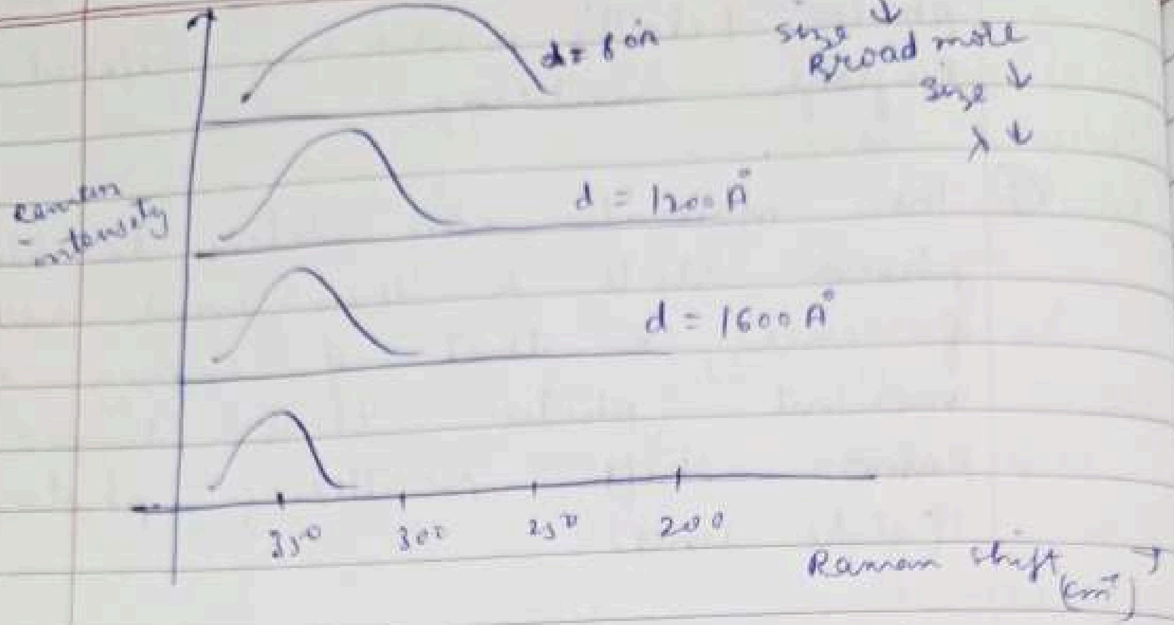
① The molecule can relax back to the ground state & emit photon of equal energy as that of incident photon (elastic process) is refered as Rayleigh scattering.

② The molecule can relax to real phonon state & then emit radiation of energy < that of energy of incident photon. It is termed as Raman shift scattering photon (stoke lines)

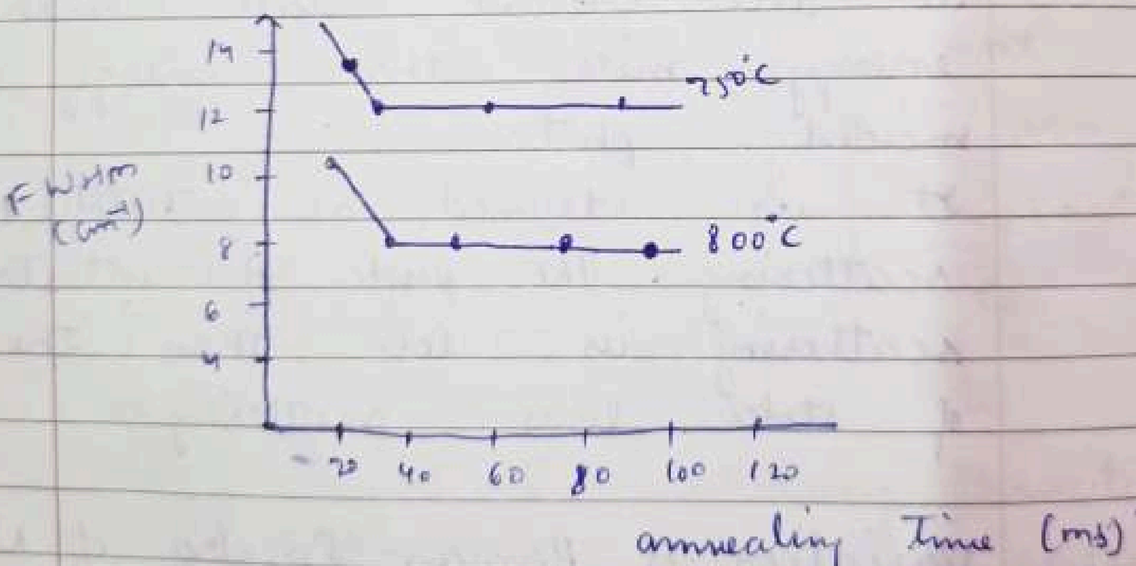
③ The third ptl outcome is that in which molecule is already in excited state. This molecule return to the ground state with energy more than energy of incident photon.
It is termed as antistoke Raman scattering. The prob. of antistokes scattering is less than the prob. scattering of stoke lines scattering.

Variation of Raman Spectra of Nano-materials

Consider the raman spectra of ~~Geram~~ Germanium nano crystal which is produced by gas condensation showing broadening & shifting of given wave no. as the particle size ↓ses.

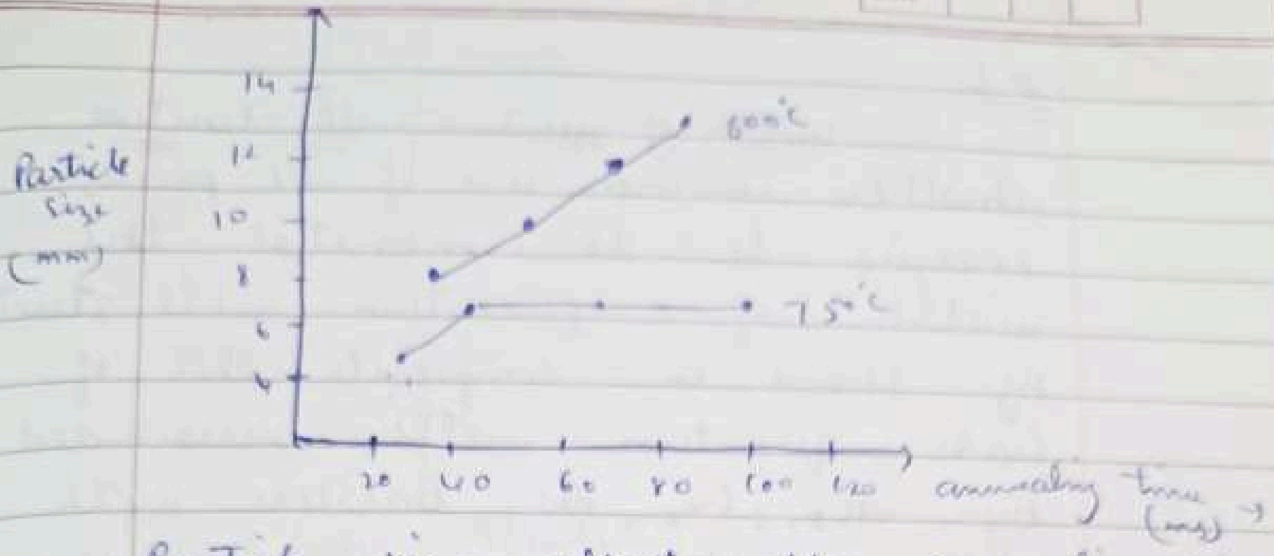


Raman intensity vs. Remen shift of the Nano crystal for diffⁿ dimensions.



FWHM of the crystal against annealing time & temp.

Annealing time - heat treatment given to sample to get desired information.



Particle size affect the annealing time of he crystal.

Application of Raman Spectroscopy

① It is used to verify raw materials.
② used to identify impurities of given sample.
③ used to analyze skin depth.
④ used to identify active pharmaceutical ingredients.
⑤ used to measuring the size of molecules less than 1 μm.

* Photoluminescence / Fluorescence spectrometry or fluorometry

Luminescence
↓
emission of light by a material through any process other than blackbody radiation.

The term photoluminescence (PL) narrows this down to any emission of light that results from optical stimulation.

In molecular systems, we use diff^n terminology to distinguish b/w certain PL processes that tend to be fast (sub-microsecond), whose emission we call fluorescence & other slower ones which are said to generate phosphorescence.

Basic Principle

In PL, a material gains energy by absorbing ~~of~~ light at some λ by promoting an el$^{\ominus}$ from a low to a higher energy level. This may be described as making a transition from ground state to an excited state of an atom or molecule, or from V.B. to C.B. of a S/C crystal (e-h pair creation).

After a system dependent characteristics lifetime in the excited state, which may least from picoseconds to many seconds, the el$^{\ominus}$ system will return to the ground state. In luminescent materials some or all of the energy released during this final transition is in the form of light, in which case the relaxation is said to be radiative. The wavelength of this emission is longer than that of the incident light.

This emitted light is detected as photoluminescence & the spectral dependence of its intensity is analyzed to provide information about the prop. of the material.

<u>empirical relation</u>.

$$\underset{\text{emission}}{\hbar\omega} = E_{g(\text{bulk})} + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

λ can be calculated

$$\underset{\mu m}{\lambda} = \frac{1.24}{E_g\,(\text{eV})}$$

Size of Nano particles

$$E_{g,nano} = E_{g,bulk} + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right)$$

Instrumentation

Four Basic components make up a PL system

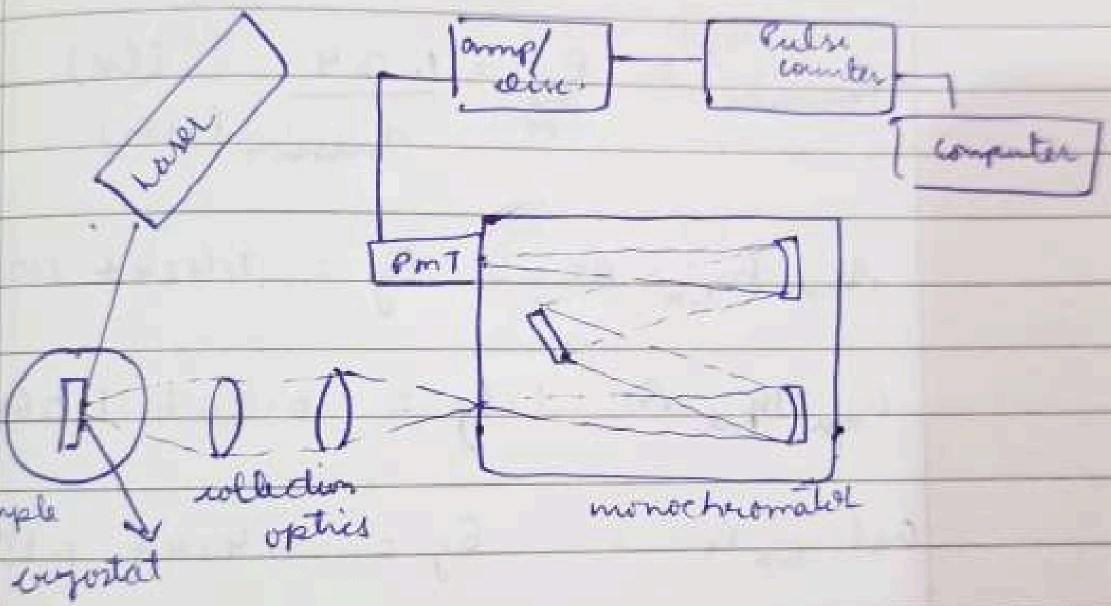
(a) A source of light for excitation. Surface studies generally require a continuous or pulsed laser. A dye or Ti: sapphire laser is used if tunability is needed.

(b) A sample holder along with optics for focusing the incident light & collecting the emitted light. It may allow for cryostat, pressure cell, magnet or electrical contacts.

(c) A dispersive element for spectral analysis of PL. This may be as simple as a filter, but it is usually a scanning grating monochromator.

(d) An optical detector with appropriate electronics & readout. Photo-

-multiplier tubes supply good sensitivity for λ in visible region & Ge, Si or other photodiodes can be used in the near infrared range. Multichannel detectors like CCD or photodiodes arrays can reduce arrangement times & a streak camera or non-linear optical technique can be used to record ps or sub-ps



Applications

Alloy composition

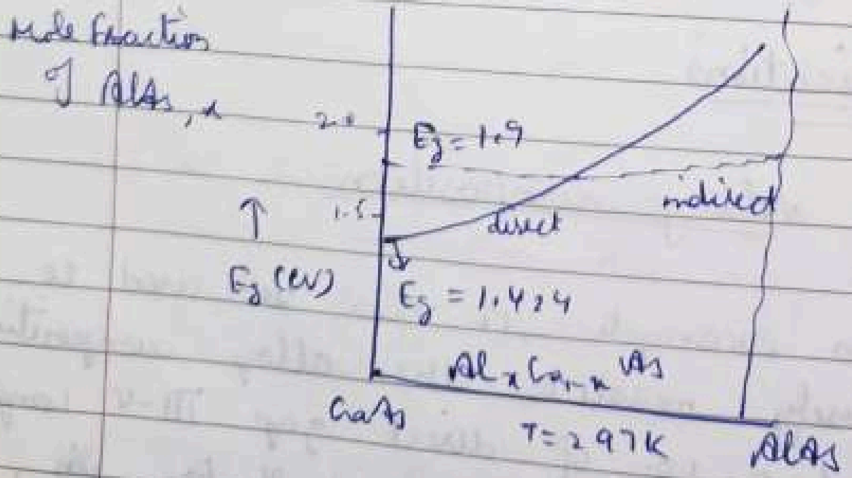
As an example, PL can be used to precisely measure the alloy composition x of a no. of direct gap III-V compound semiconductor such as $Al_xGa_{1-x}As$, $Ga_xIn_{1-x}As$ & $GaAs_{1-x}P_x$ since the band gap is related to x. This is possible in extremely thin layers that would be difficult to measu by other techniques. A calibration curve of composition vs band gap is used for quantification. Cooling the sample to cryogenic temp can narrow the peaks & enhance the precision.

$$E_{emission} = E_{band\ gap} = \frac{1.24}{\lambda_{emission}\ (\mu m)}\ (eV)$$

$Al_x Ga_{1-x} As$: $E_g = 1.424 + 1.247x$

$Ga_x In_{1-x} As$: $E_g = 0.36 + 1.064x$

$GaAs_{1-x} P_x$: $E_g = 1.424 + 1.150x + 0.176x^2$



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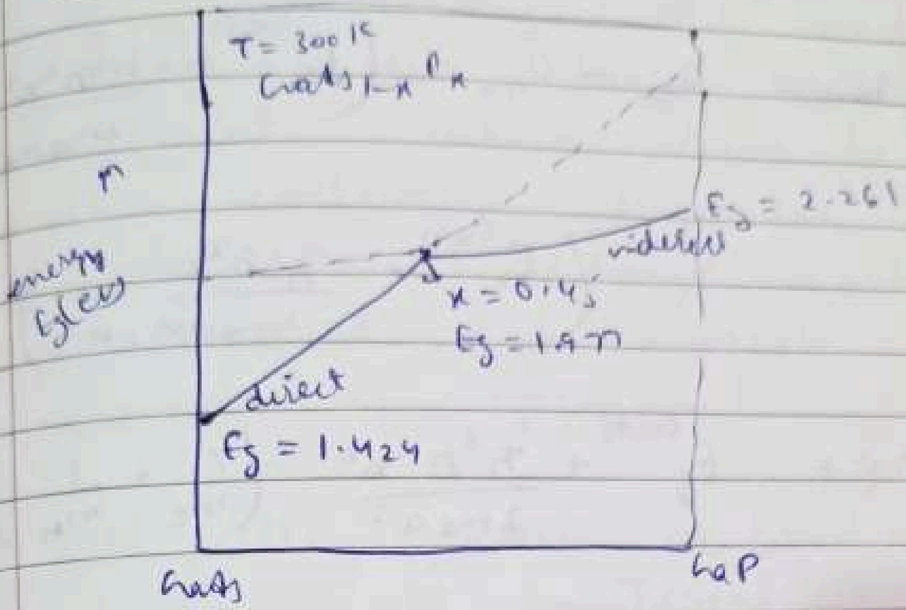
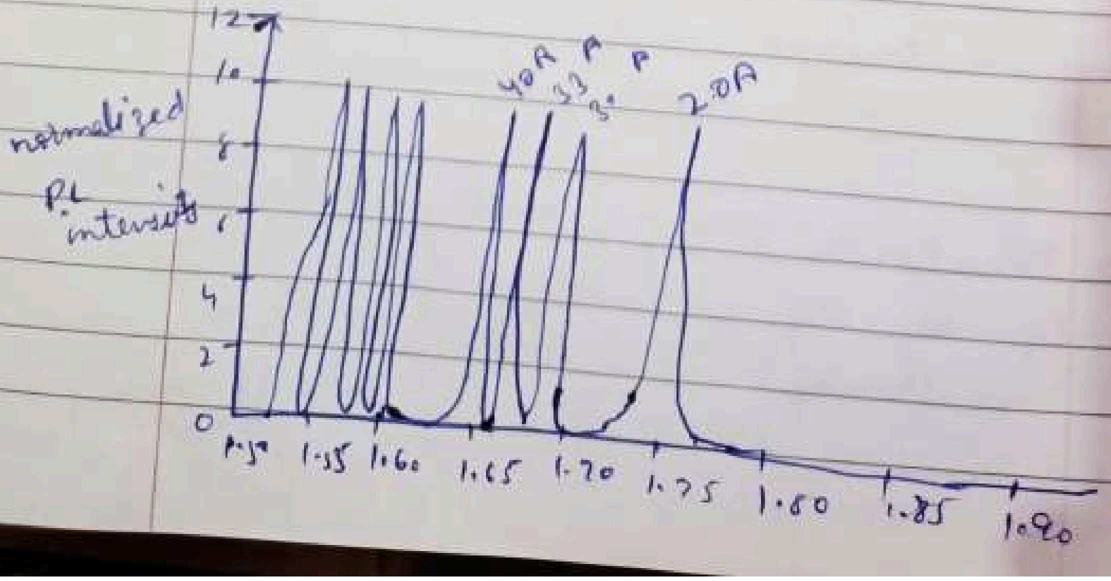
Mole Fraction of GaP, x



PL

width of quantum well structure

Another common use of PL peaks energies is to monitor the width of quantum well structure. Fig shows a composite plot of GaAs quantum wells surrounded by $Al_{0.3}Ga_{0.7}As$ barriers with well widths varying from 13nm to 0.5nm, the last being only two atomic layers thick. Each of these extremely thin layers gives rise to a narrow PL peaks at an energy that depends on it's thickness. The well widths can be measured using peak energy & a simple theoretical model. The peak energy is seen to be very sensitive to well width & the peak width can give an indication of interface sharpness.



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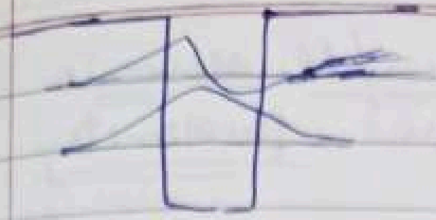

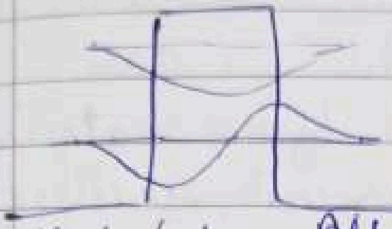

energy must be measured from the bottom of the band E_c rather than zero & energy of bound states, labeled with n_e is

$$E_{en_e} \approx E_c^{GaAs} + \frac{\hbar^2\pi^2 n_e^2}{2m_0 m_e a^2}$$

again there is a quantum well bcz E_v is at diffⁿ level in GaAs well & AlGaAs barriers ∴ The energy of bound states are:

$$E_{hn_h} \approx E_v^{GaAs} - \frac{\hbar^2\pi^2 n_h^2}{2m_0 m_h a^2}$$

strong absorption occurs at freq. given by

$$\hbar\omega = E_{cn} - E_{hn} = \left(E_c^{GaAs} + \frac{\hbar^2\pi^2n^2}{2m_0 m_e a^2}\right)$$

$$- \left(E_v^{GaAs} - \frac{\hbar^2\pi^2n^2}{2m_0 m_h a^2}\right)$$

$$\hbar\omega = E_g^{GaAs} + \frac{\hbar^2\pi^2n^2}{2m_0 a^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right)$$

ħ ω can be can be noted from PL spectroscopy & other parameters are const & hence well width 'a' can be calculated.

size of nano

$$E_g^{nano} = E_g^{bulk} + \frac{\hbar^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h}\right)$$

$$E_g^{bulk} + \frac{3h^2}{8L^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h}\right) \qquad \boxed{n^2 = n_x^2 + n_y^2 + n_z^2}$$

$$E_{x} = E_g^{bulk} + \frac{\hbar^2\pi^2n^2}{2m_e^* L^2}$$

Ball - N
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Ball - Milling

It is a top down approach of synthesising the nanomaterials, use large initial material which can be externally controlled in the processing of nanomaterials (large scale which is reduced to nanoscale after a sequence of operation)

→ Ball milling process is based on grinding of material.

→ A Ball mill is the type of grinder viz used to grind~~er viz~~ ~~used~~ the raw material into super-fine powder & mixing the material, paints, Pyrotechnique

→ It consists of hollow cylinder & ball present inside the cylinder.

→ The hollow cylinder viz rotates about its axis & the axis of cylindrical shell may be either horizontal or inclined at a small angle to the horizontal.

→ In mill whole process of size reduction depend on the speed of rotation.

→ Rubber is prefered for this purpose due to less wear in mills lined with rubber.

Page No.
Date

Construction

↓ It consists two parts

↙ ↘

Hollow cylinder   Balls.

→ **Hollow cylinder** :- It is made up of metals. The inner surface of cylinderical shell is generally lined with an abrasion (friction) resistant material e.g. rubber or mangenese steel.

→ length & dia. of balls nearly equal

→ the hollow cylinderical shell is attached to ~~nott~~ metallic frame & these metallic frames allows the rotation of the hollow cylinder at its axis

→

→ **Balls** :-

The balls are also made up of metal & other material like steel, chromium, stainless steel, ceramic or rubber

→ these balls form the grinding media of the ball mill.

→ the wt of balls are equal

→ the ball size depends on size of the mill size
&
(cylinderical shell)

up of
ner surface
generally
sion (friction)
rubber or

arly equal.
shell &
c frame
allows the
cylinder

made up of
like
less steel,

nding media

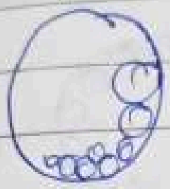
ual
size of

Principle

A ball mill work on the principle of 'impact' & 'attrition'.

attrition
↓
friction
↓
b/w material particle

impact
↓
collision
↓
one obj hitting another (a slid particle b/w balls)



→ at rapid speed impaction occur as the moving balls hits the material, that comes in b/w them while the attrition occurs at low speed by the balls moves together.

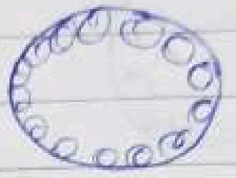
Working :- the speed of ball mills is of 50 rpm. by the process of size reduction totally depend on it.

① The raw material is to be grinded put into ball mill compound fill in cylinder upto 60-65% of total vol. of cylinder, the metal ball is fill upto 35-40%.

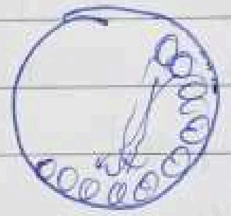
② then the mill is allowed to rotate

→ The speed of rotation is very imp.
bcz at the low speed rols over each other (

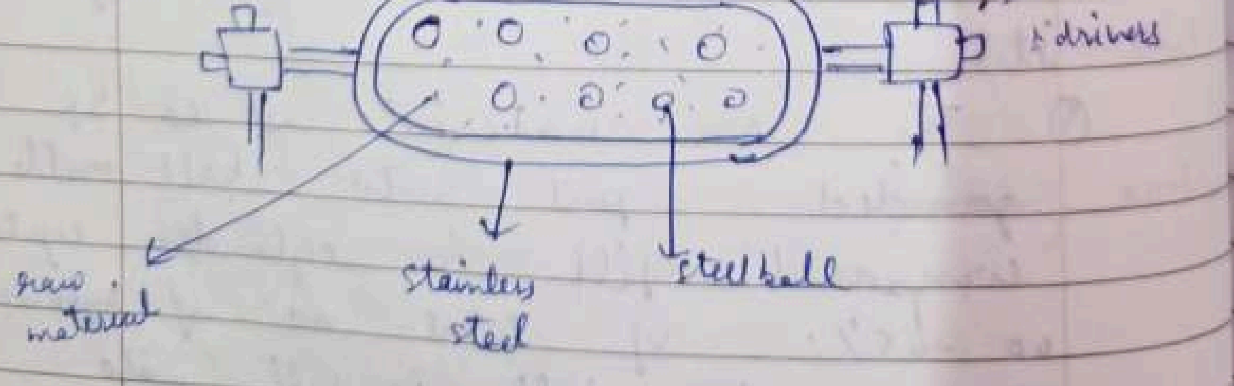
→ If rot. speed is high, due to high speed centripital force material of balls sit on the wall of the cylinder



∴ So, the ball mill operates at correct speed.



dia:-



→ highly quality ball mills are potentially expensive & can grind mixture particles do as small as 5nm. which enormously ↑se the surface area & rex^n rate.

→ There are 2 types of ball mill grate type & overfall type acc to ~~in~~ diff ways of raw material

→ large sized mills are mechanically rotated on their axis.
but small mills normally consists of a cylinderical capped container that sits on two drive shafts

motor are used in external source type

→ Planetary ball mill:- is smaller than a common ball ~~mill~~ mill & is generally used in laboratories for research purpose

App: A ball mill can be used for grinding material such as ores, chemicals, ceramic raw material & paints

→ are used in pyrotechniques & the manufacture of black powder

Pyrotech → flash powder (पटाखे)

Chemical Bath/Solution Deposition

- CBD technique involves controlled precipitation of a compound form the solution on suitable substance.
- The first CBD thin film were prepared in 1884 & this method was limited to PbS & PbSe for a long time.
  ↓ lead sulphide (PbS)
  ↓ lead Selide (PbSe)
- After the deposition of CdS a wide range of chalcogenide & chalcopyrite material (covalent bonded) have been prepared by this method
- 1980, the focus of CBD films slowly turned towards solar energy application.

Advantages of CBD

- CBD is the simplest cost effective method.
- it is possible to deposit multi-compound thin film over a wide range.
- chemical do not require high

vaccum & it can be carried out even at room temp

→ inexpensive method for large scale industrial application

→ crystal size of the CBD films is very small.

Principle :-

→ In this technique it is possible to control the film thickness & chemical composition by varying the deposition parameters such as temp., precursor ions, complexing agent & the pH of solⁿ.

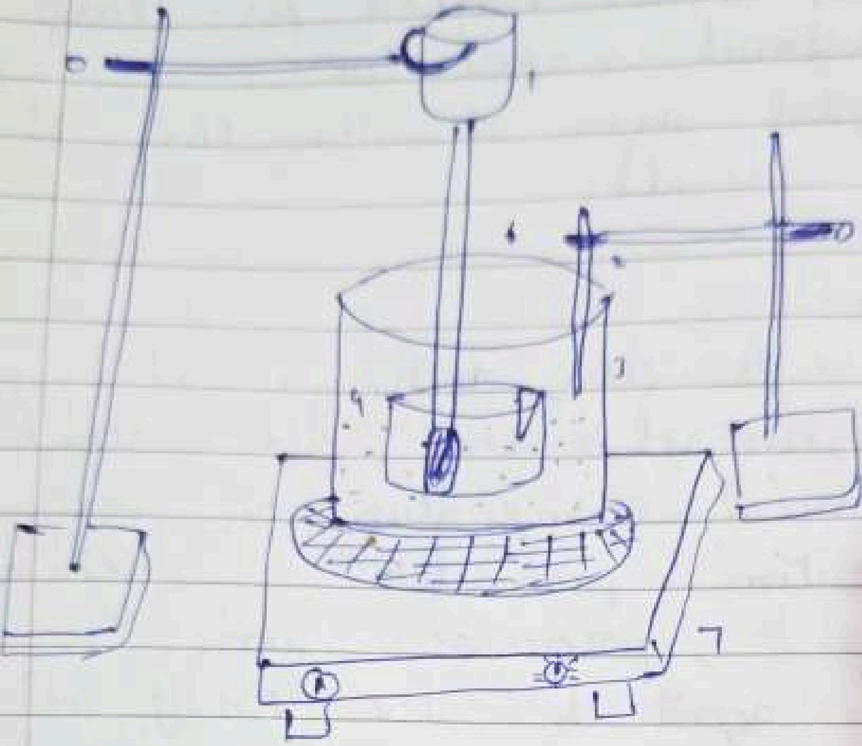
→ The ability of this method to coat large areas in a reproducible & low cost process.

→ this method depend on the deposition of thin films from aqueous solⁿ either by passing a current or by chemical reaⁿ

Imp → In CBD process thin films are deposited on a solid substrate when it is immersed into a dilute solⁿ of one or more metal salts

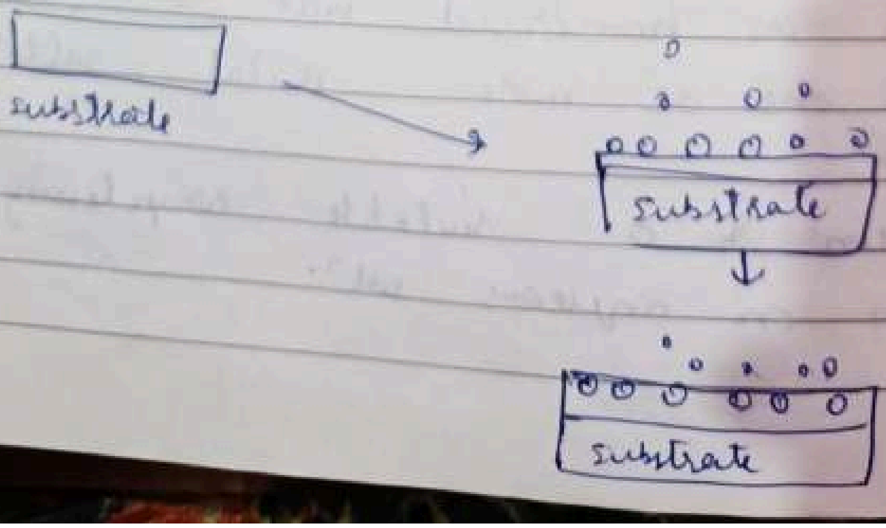
→ ion & a suitable complexing agent in an aqueous solⁿ.

→ The block dia. of CBD method



1) motor 2) thermometer
3) water bath 4) glass beaker
5) glass slide
7) heater

⊛ Various process of thin film deposition in CBD technique



→ ion by ion process
→ cluster by cluster process.
→ mixed process

⇒ This method the metal chalcogenide films will form on substrate [illegible] by 4 steps
(i) eqm b/w water & complexing agent
(ii) formation of metal complex species.
(iii) hydrolysis of the chalcogenide ~~st~~ source.
(iv) formation of solid film on the substrate.

⊙ The deposition of films occurs on substrate when the value ionic product exceeds the solubility product, otherwise it is precipitated out.

→ The basic principle of CBD is ~~the~~ to control the chemical rexn.
→ commonly used complex agent

element	com. agent
Fe	TEA, NH_3
Ag	CN^- NH_3 Cl^-
Cd	CN^- NH_3 Cl^- $C_4H_4O_6^-$

Factors influencing the deposition Process

→ bath temp.
→ nature & conc. of the precursors.
→ nature & conc. of complexing agent
→ pH of solⁿ
→ deposition time
→ nature of substrate

① Bath temp. :- An imp. factor that influence the rate of rexⁿ is bath temp.
Temp. ↑ses dissociation of complex agent ↑ses & the K.E. of molecules also ↑ses.
this results ↑ses or ↓ses in the
⑤ films thickness depend on the solⁿ

② Nature ~~& conc.~~ of complexing agent has greater influence on the final product
eg. when EDTA is used as complexing agent for FeS_2 thin film preparation it was found that marcasite can + iron pyrite other phase

③ pH :- when pH of rexⁿ bath ↑se the metal complex. They will ↓se the rexⁿ rate resulting in higher thickness

ecursors.
ing agent

that
rex^n is

omplex
molecules

The
the sl^n

agent
the final

complexing
preparation
cm
epite.

se the
the
thickness

---

of the film

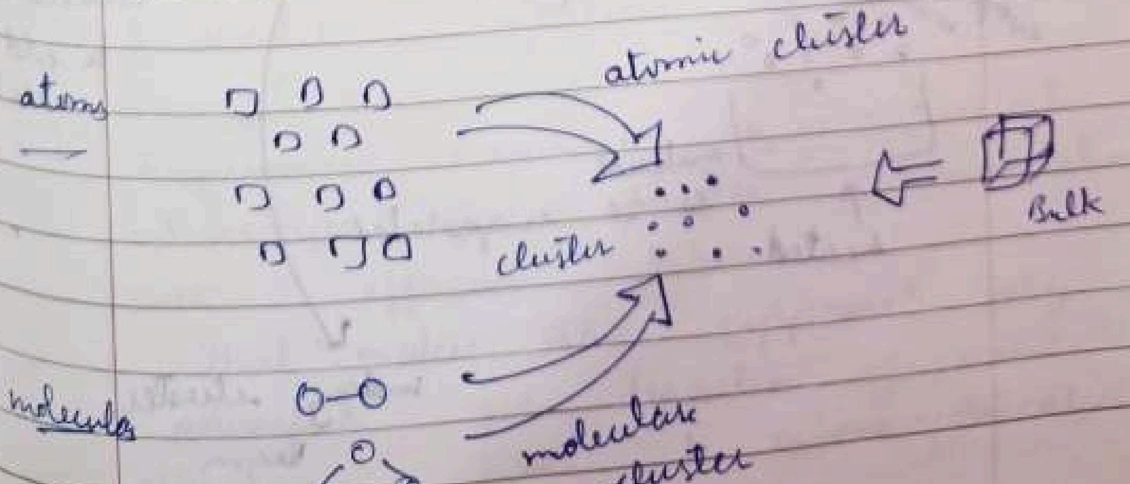
(4) Deposition Time:- The growth of good quality thin films proceeds at slow rate
The CBD method is suitable for producing uniform thickness in range of 0.05 - 0.3 µm

Cluster Beam Evaporation

(bottom-up approach) It is basically a physical vapour deposition technique which is used to deposit thin films & growth of nanostructure of materials.

cluster → few hundred to few dozens of atom together bound by some force are called cluster

Cluster can be made using atoms or molecules & bulk

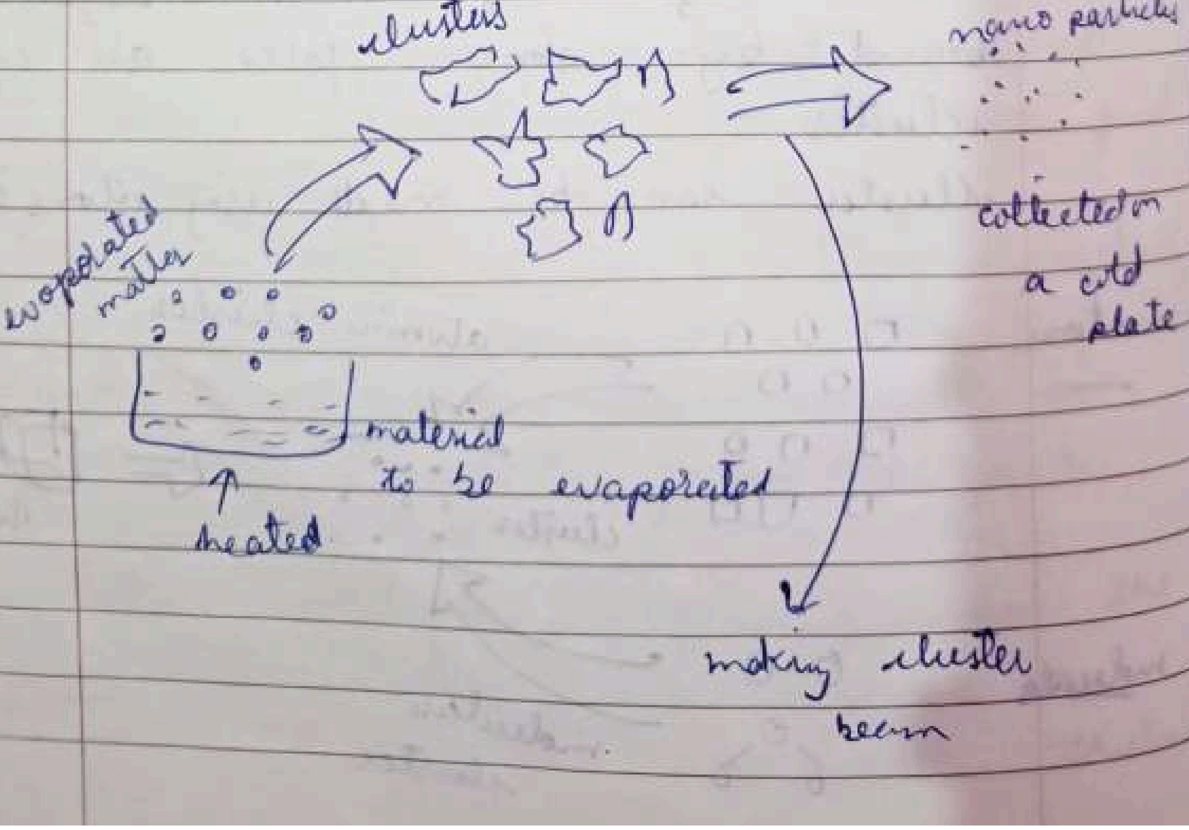


cluster can be in pure form or in mixed form.

- → Size of constituting Å to nm
- → no. of particles / constituting 2 to several thousand

- → CB.D is a method of synthesis of nanostructure material
- → it is a special type of PVD (Physical vapour deposition technique) this can be finally used to grow~~th~~ thin film nanostructure materials.

- → high degree of purity & exact nanoparticle size control



→ Aggregates ranging from a few atom to a few thousand of atom are known as clusters are produced & carried in supersonic expensions

→ cluster tells about the solid behaviour

@ A supersonic expension is achieved when high press. (1 - 6 atm) gas is expanded through a small orifice (400 - 1200) micron into a vacuum.

→ electronic structure & the lattice structure of material play an imp role in determining the stability of the cluster

→ CBD has greater ptl. for production of nanostructure & nano-composite films.

→ it is type of bottom-up approaches & used in synthesis of nano materials

→ Supersonic expension have several advantages for cluster manipulation over effusive beam. That makes this approach very powerful for deposition of nano structure films & micro-fabrication technique

→ a cluster may also be defined as an ensemble of bound atoms or molecules that is intermediate in size b/w molecule & a bulk.

→ cluster can also consist solely of a certain kind of molecule such as water cluster

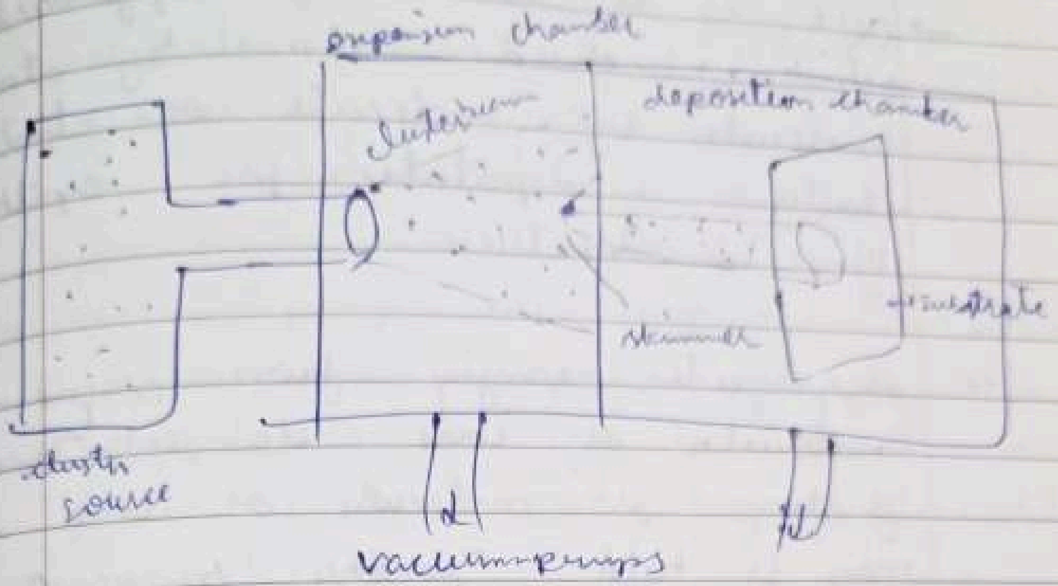
→ atomic cluster can be either pure formed, from a single atomic species or mixed formed from mixed atomic species.

→ In gas phase synthesis nanoparticles are made by individual atom & molecule up to the desired size

→ cluster embryos are formed by condensation of a supersaturated vapour or by chemical rxn

C → atom form fullerene
B → Boron cluster

expt. setup



high pres ⟶ low pres.
(supersonic expansion)

$$\frac{dD_p}{dt} = \frac{2v(P_1 - P_d)}{(2\pi m k_B T)^{1/2}} \quad F_1$$

D_p = particle diameter

T = temp.

v_1 = vol. , P_1 = partial pres. of gas

P_2 = " " at particle surface

F_1 = Fuchs . sutugin

In the continuum regime the rate of change of particles dia.

$$\frac{dD_p}{dt} = \frac{4 D v_1 (P_1 - P_d) F_2}{D_p k_B T}$$

D = diffusion coff. of gas or vapour

→ CBE is a bottom-up approach which involved atoms by atoms, molecule by molecule or cluster by cluster manipulation for synthesis of nanostructures

→ Aggregates ranging from a few atoms or molecules or ions to few thousand of atoms or molecules or ions which may be held together by various types of binding force with B.E b/w a few tenth of ev to several ev are known as cluster. & are produced & carried in supersonic expansion in which a high press gas is expanded through small orifice into vaccum.

working → In expansion chamber, the cluster beam from the cluster source undergoes supersonic expansion through the small orifice provided in the expansion chamber.

→ The central part of cluster beam enters to 2nd (deposition) vaccum chamber through the skimmer which is used for the geometrical confinement of cluster beam.

→ Now, the cluster beam impinges on the substrate placed in deposition chamber & hence by cluster beam deposition on the substrate, nanoparticles are formed.

- vaccum pump are provided to create vaccum in expansion & deposition chambers so as to create low press. & to avoid any undesirable impurity.

The process of deposition of nanoparticle on substrate involves 2 processes:-

① Particle Formation
② " Growth

① <u>Particle formation</u> :- The starting material is vapourized from a hot source into a gas of low density using joule heating, thermal plasma or laser ablation. Rapid cooling of vapour leads to supersaturation followed by homogenous nucleation with the formation of 1st product cluster.

② <u>Growth</u> :- The newly formed particle continue to grow either by surface growth (addition of atoms of molecules or particles) or by coagulation (in elastic particle → collision) is generally followed by coalescence (merging of 2 or more particles on contact to form single particle)

The particle shape may be affect the rate of particle growth by coagulation

in formula

→ If the particle dia. is much smaller than the mean free path of gas, as it usually the case with clusters. The coagulation theory of free molecular regime has to be applied.

The above 2 processes usually take place simultaneously.

advantages :- ① gives high degree of purity

② gives exact particle size control.

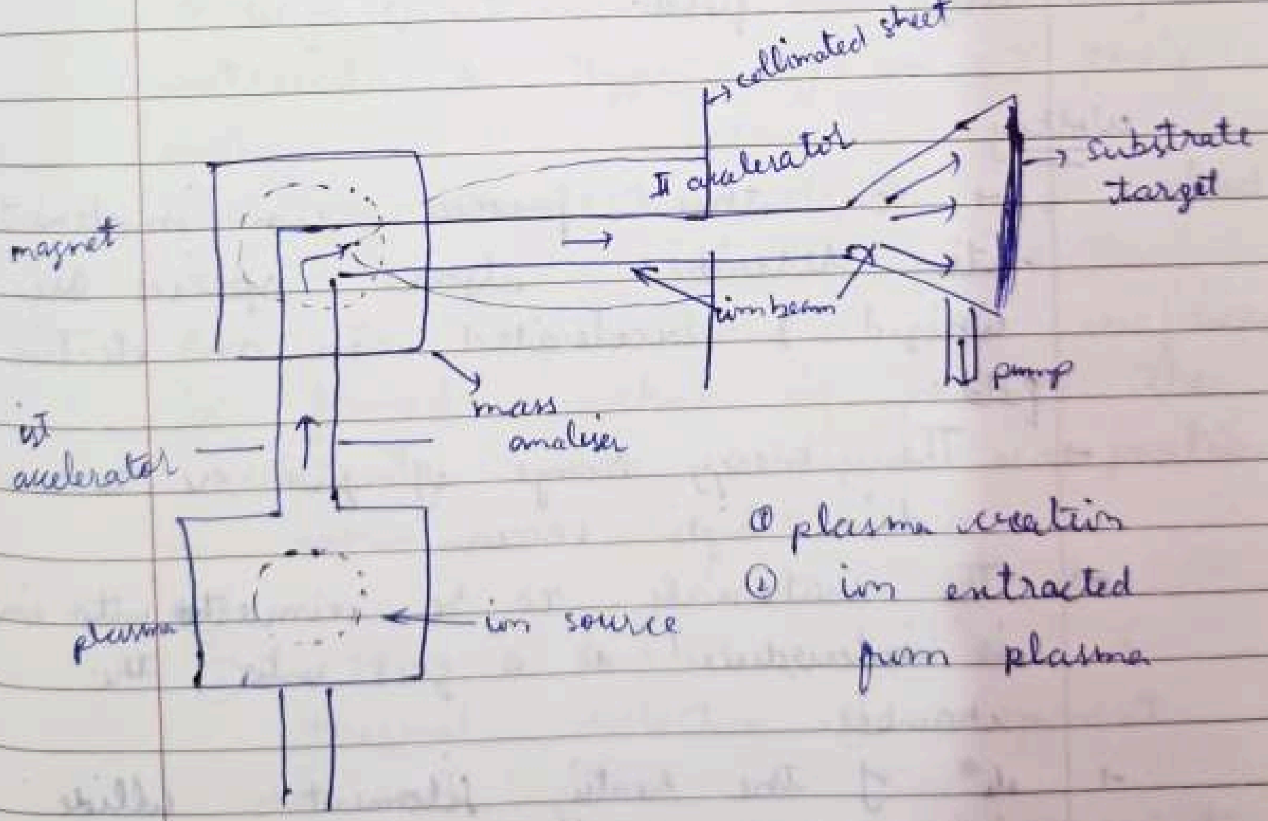
→ has high stability, repeatability, high lateral resolution & ||'el focussing.

Ion Beam Deposition (Bottom-up)

→ This is bottom-up approach for the synthesis of nanomaterials.

→ ~~The~~ A thin film deposition method that produces the high quality film with excellent precision & tight control over film thickness.

→ IBD is a process of applying material to a target through the application of an ion beam



① plasma creation
② ion extracted from plasma

→ An ion beam deposition apparatus typically consists of an ion source, ion optics & the deposition target.

- → optimalty a mass analyzer can be incorporated.
- → In the ion source, source material in the form of gas or evaporated solid or a solⁿ (liq.) are ionized.
- → For atomic ion IBD, ele⊖ ionization, field ionization or cathodic arc source are used.
- → cathodic arc sources are used particularly for carbon ion deposition.
- → The ion are then accelerated, focused or deflected using high vol. or mag field.

Working :-

- → In this process ion implementation described atomic species are ionized & accelerated in an electric field.
- → The energy range of few eV to 500 eV under high vaccum.
- → The materials to be converted into ions is introduced as a gas into the chamber.
- → ele⊖ of the heating filament collide with the atom of gas ionizing them.
- → mag. field & electric field are ↑es the efficiency of ion process & confine the plasma. Only ion of

single type energy are deflected by precisely 90° other follow slightly diffⁿ trajeaitories that separate them from beam.

→ Thus purified beam is focused & accelerated to high energy & penetrate the surface layers of substance target resulting the change in its composition & micro structure.

→ which effect the material property

→ The penetration depth range from 0.01 – 1μm which depend on the target materials & types of ion & their energy.

→ The avg. penetration depth is called the range of ion.

→ Due to implamation a new surfaces is formed which is part of the substrate with modified composition in ~~what~~ in which atom.

adv. :-

① It is a low temp process & thermal distortion of component does not exist.

② It is used in S/C device fabrication

③ By this technique it is possible to obtain nanoparticles or compounds & alloys of more than one element.

Disadv:-

① high energy beam create some defects in the substrate material.

Field ionization:- It is the ionization of a gaseous molecule by an intense electric field, usually created by a sharp electrode at a high potential.

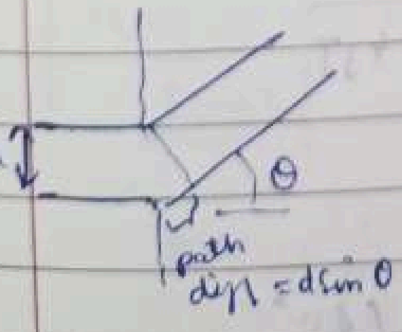
Cathodic arc source:- In cathodic arc source a high current supply to electric arc to strike & vaporize the source material within a vacuum environment.

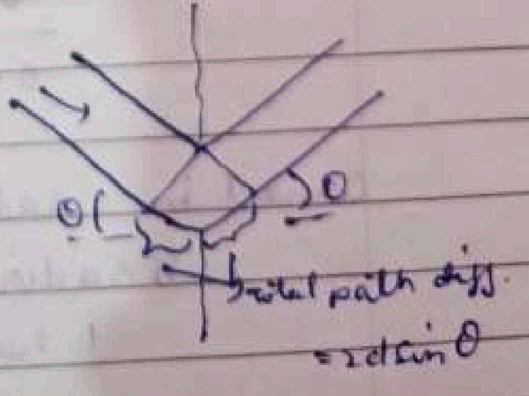
Sol /- Gel

X-ray

- → it is em radiation. X-ray are produced by bombarding high energy ele$^{\ominus}$ on heavy metal
- → Acc. to Mosley's law every element has its unique signature in form of K_α emission
- → X-ray diffract treating inter atomic dis. as slits.
- → X-ray are used over visible light for crystal diffraction bcz of its shorter λ.

- → diffraction is the main technique used to identify crystal structure.
- → when a ||'el beam diffracted from a single slit causes a path difference of $d\sin\theta$ & when incident beam is also at an angle θ then the path diff. is $2d\sin\theta$

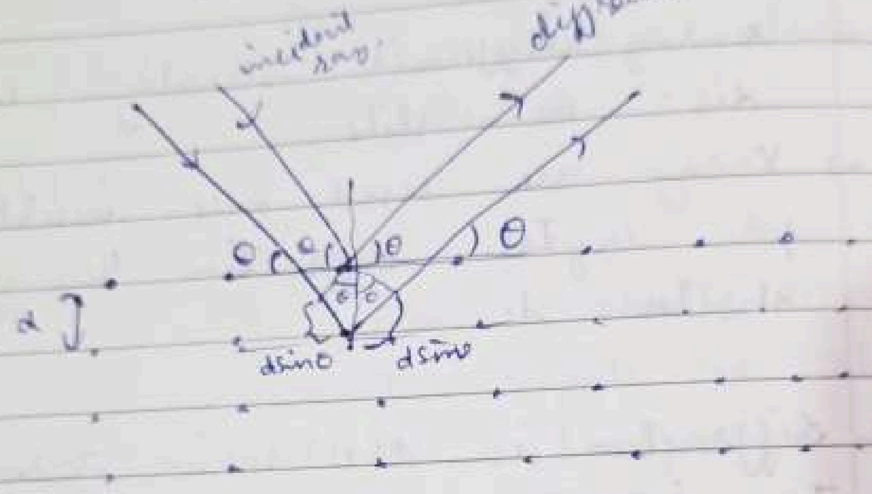




XRD

when atomic planes act as diffraction slits, then the constructive interference is defined by Bragg's law

$$\boxed{2d\sin\theta = n\lambda}$$



$$D = \frac{K\lambda}{\beta\cos\theta}$$

(Q) $\lambda = 0.15418\,nm$, $K = 0.94$

$$D_1 = \frac{0.94 \times 0.15418}{0.187 \times 0.9455}$$

convert in radian

π radians $= 180°$

1 radi $= \frac{180°}{\pi}$

degree → radian → $\times \frac{\pi}{180}$

~~$D_1 = \frac{0.94 \times 0.15418 \times 180 \times 180}{0.187 \times 3.14 \times 0.9455 \times 3.14}$~~

~~$D_1 = \frac{4695.70608}{1.7432610860} = 2693.633$ nm~~

θ → degree
β → radian

$D_1 = \frac{0.94 \times 0.15418 \times 180}{0.187 \times 3.14 \times 0.9455}$

$D_1 = \frac{26.087256}{0.55517165} = 47.277$ nm

⑮ $\lambda = 0.154$ nm   a = ?
K = 0.91   size = ?
FWHM (β) of max intensity = 0.56°

2θ	40.3	58.3	73.2	131.2
hkl	110	200	211	321
inter	(100)	15	23	18

$$D = \frac{K\lambda}{\boxed{\beta}\cos\theta}$$

$$a^2 = \frac{\lambda^2}{4\sin^2\theta}(h^2+k^2+l^2)$$

function *i.e.*, work required to pull an electron from the metal is given by

Potential energy box (3D)

Fig. 2.2. Physical model for metal

$$W = V_0 - E_F \qquad \ldots(1)$$

where W represents the energy difference between an electron at rest inside the metal and one at rest in vaccum and E_F is the **fermi energy** of the metal.

2.1.1. Free Electron Gas in One Dimension

The possible electronic energy states in potential energy box and distribution of these electrons in various energy levels are determined using quantum (Fermi-Dirac) statistics.

Let us consider a particle of mass m moving in straight line along the x-axis in one dimensional (1-D) box (see fig. 2.3). The particle is confined to move between $0 < x < L$. The potential function within the box is assumed to be zero and at the boundaries, it is infinitely large *i.e.*

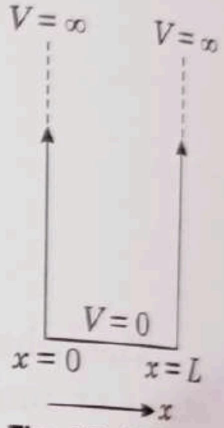


Fig. 2.3. 1-D box

$$\left.\begin{array}{ll} V(x) = 0 & \text{for } 0 < x < L \\ \quad\;\; = \infty & \text{for } x \le 0 \text{ and } x \ge L \end{array}\right\} \qquad \ldots(2)$$

The electron is confined to remain always within the potential box and wave function ψ of the electron corresponding to energy E is determined from Schroedinger wave equation as

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \qquad \ldots(3)$$

where E is kinetic energy of the electron. The general solution of this equation is

$$\psi(x) = A\sin kx + B\cos kx \qquad \ldots(4)$$

where A and B are constants to be determined from the boundary conditions and

$$k=\sqrt{2mE/\hbar} \qquad \text{...(5)}$$

Boundary conditions are (due to continuity of ψ),

$$\left.\begin{aligned}\psi &= 0 \text{ at } x=0\\ &= 0 \text{ at } x=L\end{aligned}\right\} \qquad \text{...(6)}$$

Putting $\psi(x)=0$ when $x=0$ in eq. (4), we get

$$\psi(0)=A\sin k.0+B\cos k.0$$

$$0=0+B\times 1$$

or

$$B=0 \qquad \text{...(7)}$$

Using $\psi(x=L)=0$, eq. (4) yields

$$\psi(L)=A\sin k.\mathrm{L}=0$$

$A\neq 0$ (otherwise $\psi(x)=0$ for all values of x), hence

$$\sin k.\mathrm{L}=0$$

or

$$k=\frac{n\pi}{L} \qquad \text{...(8)}$$

where $n=1, 2, 3....$. Thus the eq. (4) for the allowed wave function becomes

$$\psi_n(x)=A\sin\left(\frac{n\pi}{L}\right).x \qquad \text{...(9)}$$

The **allowed energy values** or **eigen values** can be obtained from equations (5) and (8) as

$$k=\frac{n\pi}{L}=\sqrt{\frac{2mE}{\hbar^2}}$$

or

$$E_n=E=\frac{n^2\pi^2\hbar^2}{2mL^2} \qquad \text{...(10a)}$$

$$E_n=\frac{n^2h^2}{8mL^2} \qquad \text{...(10b)}$$

$$\therefore \quad E_n\propto n^2 \qquad \text{...(11)}$$

A graph between E_n and n is shown in fig. 2.4. It shows that the energy levels of particle (here, electron) confined within the box are **quantized or discrete**. The spacing between energy levels depend upon n and L, where n is known as **quantum number**. Thus confinement of electron leads to quantization of its energy levels.

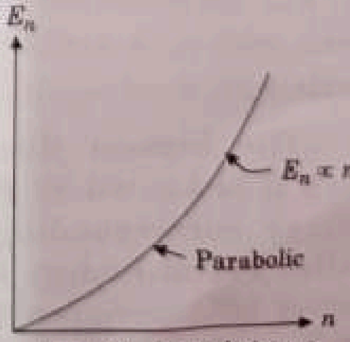


Fig. 2.4. Graph between E_n and n

To evaluate the value of A, we normalize the wave function $\psi_n(x)$ for which

$$\int_0^L \psi_n^*(x)\,\psi_n(x)\,dx=1$$

or $$A^2\int_0^L \sin\left(\frac{n\pi}{L}x\right)\sin\left(\frac{n\pi}{L}x\right)dx=1$$

or $$\frac{A^2}{2}\int_0^L \left[1-\cos\left(\frac{2n\pi}{L}x\right)\right]dx=1$$

or $$\frac{A^2}{2}\int_0^L dx=1$$

or $$\frac{A^2}{2}.L=1 \quad \text{or} \quad A=\sqrt{\frac{2}{L}}$$

Substituting it in eq. (9), we get

$$\psi_n(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}\right)x \qquad \ldots(12)$$

First three energy levels and **eigen functions** corresponding to $n=1, 2, 3$ are shown in fig. 2.5.

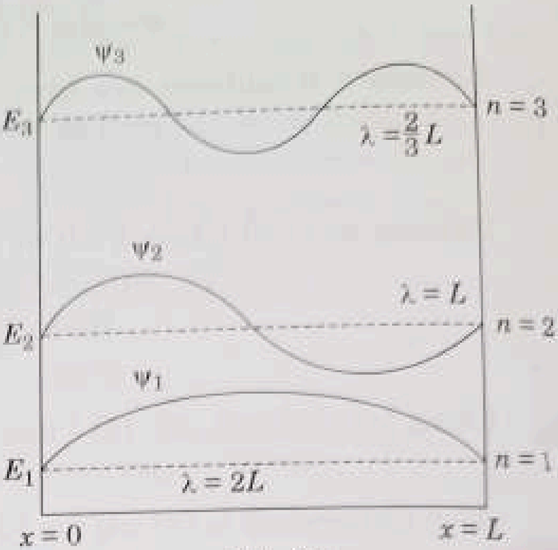


Fig. 2.5.

2.1.2. Fermi Energy

We know that free electrons in a crystal or metal are distributed among various discrete energy levels in accordance with Pauli's exclusion principle, according to which **no two electrons can be in the same quantum state**. In other words, if one electron is in a specific quantum state, the other electron must then be in a different quantum state.

In a metal, an electron in an energy state is specified by n (principal quantum number) and m_s (magnetic spin quantum number). One quantum state denotes one set of values of n and m_s. There are two possible values of m_s ($\pm 1/2$) for each value of n. Hence each energy level corresponding to principal quantum number n can have two quantum states ($m_s = \pm 1/2$) and hence can accommodate a maximum of two electrons – one of spin up $\left(i.e., m_s=+\frac{1}{2}\right)$ and other of spin down $\left(m_s=-\frac{1}{2}\right)$.

Fig. 2.6 shows the filling up of 7 electrons in different energy levels. The energy levels with $n \le 4$ would be occupied while the levels with $n > 4$ would be empty.

"The highest filled energy level at $T = 0$ K is known as Fermi level and the energy corresponding to Fermi level is called Fermi Energy E_F". In this case, the energy level corresponding to $n = 4$ is known as Fermi level.

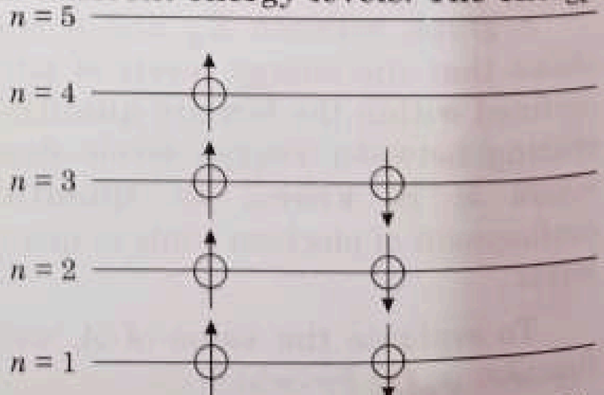


Fig. 2.6. Filling of electrons in various energy levels

If N is the total number of electrons to be accommodated, then if n is even, we can write

r² radius of n-space line (1D) = N
r² radius of n-space circle (2D) = N
r² radius of " " sphere (3D) = N
→ N = 2 no. of states

$$2n_F = N \qquad \text{...(13)}$$

where n_F is the principal quantum number of the Fermi level. Hence for $n = n_F$, eq. (10) becomes

$$E_F = \frac{\hbar^2}{2m}\left(\frac{n_F .\pi}{L}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{N.\pi}{2L}\right)^2 \qquad \text{...(14)}$$

$$= \frac{\hbar^2}{2m}\left(\frac{\pi N}{2L}\right)^2 = \frac{h^2}{2m}\left(\frac{N}{4L}\right)^2$$

where (N/L) is the number of electrons per unit length. For 3-D metallic crystal (*i.e.*, a cubical box), the eqn. (12), (10) and (14) transform respectively as

$$\psi(r) = \sqrt{\frac{8}{L^3}}\sin\left(\frac{\pi n_x x}{L}\right)\sin\left(\frac{\pi n_y y}{L}\right)\sin\left(\frac{\pi n_z z}{L}\right) \qquad \text{...(15)}$$

$$E_n^2 = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) \qquad \text{...(16)}$$

doubles no.

$N = 2\left(\frac{4}{3}\pi n_F^3\right) \times \frac{1}{8} \rightarrow$ for +ve value

where $n^2 = n_x^2 + n_y^2 + n_z^2$.

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \qquad \text{...(17)}$$

(from value of no. of states (N))

where n_x, n_y and n_z are positive integers, $\sqrt{\frac{8}{L^3}}$ or $\sqrt{\frac{8}{V}}$ is the normalizing constant and V is the volume of the 3-*D* box or crystal.

2.1.3. Density of (Electronic) States

density of states in Band

"The total number of available electronic states per unit energy interval is known as density of states". The density of states is denoted by $g(E)$ and is given by

$$g(E) = \frac{dn}{dE} \qquad \text{...(18)}$$

where dn is the number of electronic states present in the energy range E to $E + dE$.

According to free electron theory of metals, each energy level contains two electronic states, one with spin up and the other with spin down, therefore

$$g(E) = 2 \times \frac{dn}{dE} \qquad \text{...(19)}$$

From eq. (10a), we have

$$E = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

or
$$\frac{dE}{dn}=\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2\times 2n=\frac{n\,h^2}{4\,mL^2} \qquad \because \quad \hbar=\frac{h}{2\pi}$$

or
$$\frac{dn}{dE}=\frac{4mL^2}{nh^2}$$

Substituting this value in eq. (19), we get
$$g(E)=\frac{2\times 4mL^2}{nh^2}=\frac{8mL^2}{h^2}\times\frac{1}{n}$$

Again from eq. (10a), we have
$$E=\frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2=\frac{n^2h^2}{8\,mL^2}$$

or
$$\frac{1}{n}=\left(\frac{h^2}{8mL^2E}\right)^{1/2}$$

Hence,
$$g(E)=\frac{8mL^2}{h^2}\times\left(\frac{h^2}{8mL^2\,E}\right)^{1/2}$$
$$=\frac{4L}{h}\left(\frac{m}{2E}\right)^{1/2} \qquad \text{...(20)}$$

$\therefore$
$$g(E)\propto\frac{1}{\sqrt{E}}$$

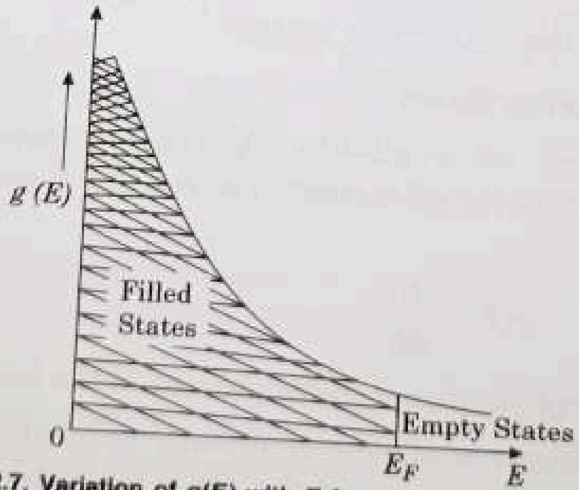
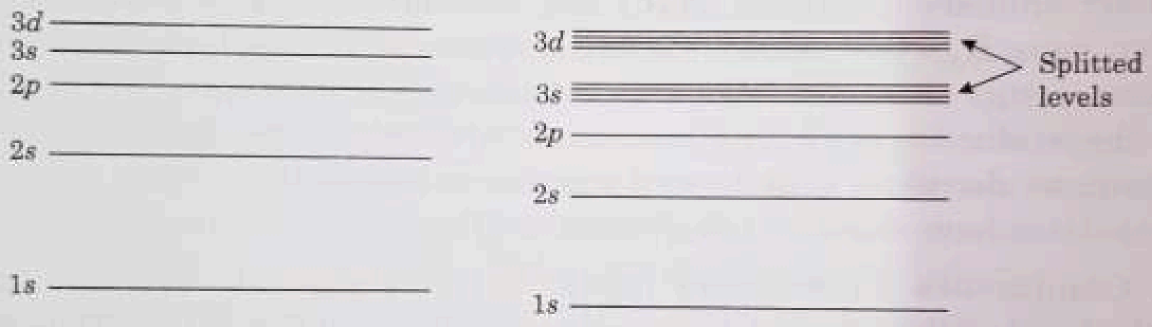


Fig. 2.7. Variation of $g(E)$ with E for a 1-D metallic crystal

Fig. 2.7 shows the variation of density of states $g(E)$, with energy E and it indicates that all energy levels upto E_F are filled with electrons.

2.2. THE BAND THEORY OF SOLIDS

We know that electrons in an isolated atom possess discrete energy levels 1s,2s, 2p,.... etc. (fig. 2.8 a). These levels are filled with electrons in the order of increasing energy. When these isolated atoms combine to form a solid, they arrange themselves in an orderly pattern, called a crystal. In a crystal, due to periodicity, each atom is in the electrostatic field of neighbouring atoms. The discrete energy levels of individual atoms are no longer valid. Instead, due to interaction between atoms, each discrete level splits into closely spaced sub-levels (fig. 2.8b). The number of sub-levels is equal to the number of atoms N in the solid. Since N is very large ($N \simeq 10^{23}$ /cc), therefore separation between these sub-levels is very small ($\approx 10^{-23}$ eV). Hence these sub-levels are almost continuous in energy and thus are said to form **energy bands**. The first energy levels of various atoms constitute the first energy band, the second energy levels form the second energy band and so on. The energy band formed by valence electrons of atoms is called the **valence band**. This band is the highest occupied band. The next higher band is known as **conduction band** and is normally empty. Now these allowed energy bands are in general separated by regions which have no allowed energy states. Such regions are termed as **forbidden energy bands** or energy gaps.



(a) Discrete energy levels for isolated atom

(b) Energy levels of atoms in a solid

Fig. 2.8.

The splitting of energy levels does not take place for lower levels 1*s* and 2*s* because the electrons in these levels (being deep inside the atoms) are not significantly affected by the presence of other atoms. Further the 2*p* level does not begin to split until the interatomic separation becomes smaller than actually found in case of sodium. In fact 3*s* level is the first occupied level to be splitted into sub-levels. *In higher energy levels splitting occurs because electronic wave functions overlap significantly to give rise to interaction between them.* Fig. 2.9 shows the splitting of various energy levels in terms of interatomic separation.

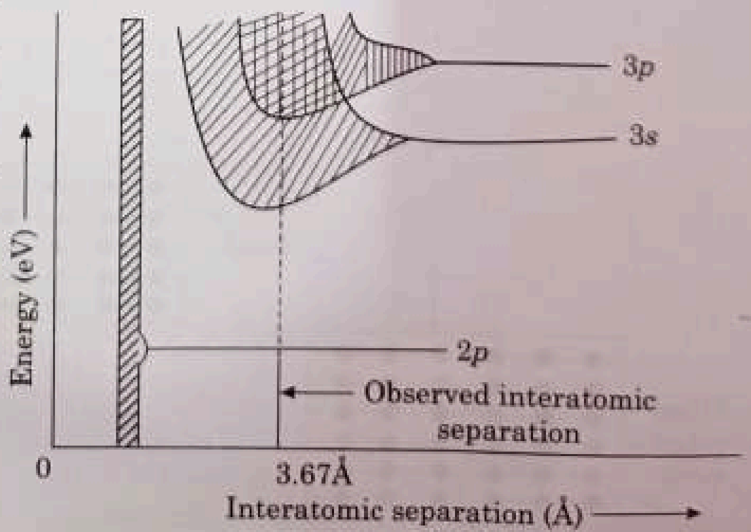


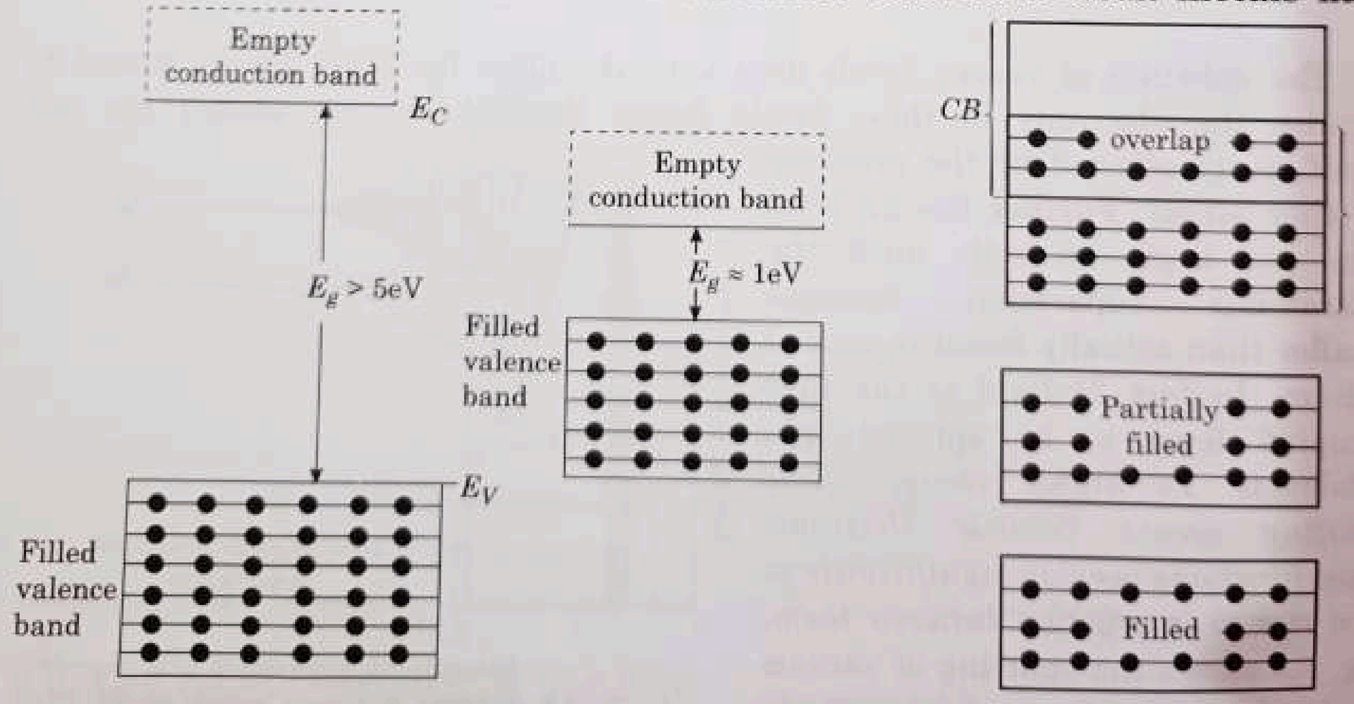
Fig. 2.9. Splitting of various energy levels

2.3. DISTINCTION BETWEEN CONDUCTORS, INSULATORS AND SEMICONDUCTORS ON THE BASIS OF BAND THEORY OF SOLIDS

The energy band structure is a characteristic feature of a solid. Thus different solids possess different band structures which gives rise to the wide range of electrical properties observed in them. Depending on the nature of band occupation by electrons and the width of forbidden energy bands, all solids can be classified into conductors, semiconductors and insulators.

I. Insulators : Insulators are those substances in which the valence band is completely filled with electrons and the conduction band is empty and there is a large forbidden energy gap (≈ 5eV or more) between these two (fig. 2.10a). Because of this large gap, electrons can not be thermally excited easily across this gap from the valence band to the conduction band. Therefore an external electric field (*i.e.* electric potential) can not cause any significant current. For this reason, the electrical conductivity of such materials is extremely small and may be regarded as zero under ordinary conditions. **NaCl** and **Diamond** are good insulators having forbidden gaps $E_g \approx 6\text{eV}$. When the temperature of an insulator is raised above room temperature some of the valence electrons may acquire enough energy to cross over to the conduction band giving rise to an extremely small current. So resistance of an insulator decreases slightly with increase in temperature. Thus the resistance of an insulator have *negative temperature coefficient of resistance.*

II. Conductors : Conductors (particularly metals) are those substances in which the bands either overlap or are only partially filled (fig. 2.10c). Thus electrons and empty energy states are intermixed within the bands so that electrons can move freely under the influence of an external electric field. As a result **metals have**



(a) Insulator (b) Semiconductor (c) Conductor

Fig. 2.10. Energy band structures at absolute zero

high electrical conductivity. However, their conductivity decreases with increase in temperature. The electrical resistance (or resistivity) of metals increases with increase in temperature due to increased number of collisions at higher temperatures. **Hence metals have a positive temperature coefficient of resistance.** Due to overlapping, the valence band also acts as the conduction band.

Consider the case of sodium ($Z = 11$). The electronic configuration of Na is $1s^2\,2s^2\,2p^6\,3s^1$. Thus the valence band (formed by $3s$ levels) is only partially filled. On application of electric field, electrons can freely move into empty states within the same partially filled band. This makes sodium a good conductor. Another metal magnesium ($Z = 12$, $1s^2\,2s^2\,2p^6\,3s^2$) is also a good conductor because in it, there is overlapping of $3s$ and $3p$ bands. Current flow is possible in an electric field.

Thus the observed electrical properties of conductors (metals) can be explained on the basis of their band structure. In fig. 2.10c, the conduction band is abbreviated as *CB*, whereas valence band as *VB*.

III. Semiconductors : The band structure of semiconductors is similar to that of insulators at absolute zero temperature *i.e.* a filled valence band separated from an empty conduction band by a forbidden gap which has no allowed energy states. However, the band gap energy E_g is much smaller in semiconductors than in insulators. For example, the semiconductor Si has a band gap of about 1.1 eV compared with 6 eV for diamond. The other popular semiconductor Ge has still smaller band gap of 0.72 eV. Due to relatively small band gaps of semiconductors, electrons may be thermally or optically excited from the valence band to the conduction band. Thus a significant number of electrons may be thermally excited across the gap into the conduction band at room temperature. As a result their resistivity decreases with increase in temperature. Hence **a semiconductor has a negative temperature coefficient of resistance**.

At absolute zero temperature, the filled valence band has no empty states into which electrons can move. Also in the empty conduction band, there are no electrons which can move into vacant energy states. Thus there will be no conduction at all on applying external electric field. **Thus a semiconductor behaves like an insulator at absolute zero temperature.** The band structure of semiconductors is shown in fig. 2.10b. Their conductivity can also be increased by the controlled addition of suitable impurities in a process called **doping.**

2.4. ENERGY BANDS AND BAND GAPS OF SEMICONDUCTORS

The important properties of semiconductors such as electrical, optical, magnetic etc. depend strongly on the manner in which energy of the loosely bound electrons depend upon the wavevector $\boldsymbol{k}$ in reciprocal (or $\boldsymbol{k}$) space. The electron momentum $\boldsymbol{p}$ is given by $p = mv = \hbar k$. Let us consider three-dimensional crystals, particularly III–V and the II–VI semiconducting compounds, which have a cubic structure ($a = b = c$). The electron motion expressed in the coordinates k_x, k_y, k_z of reciprocal

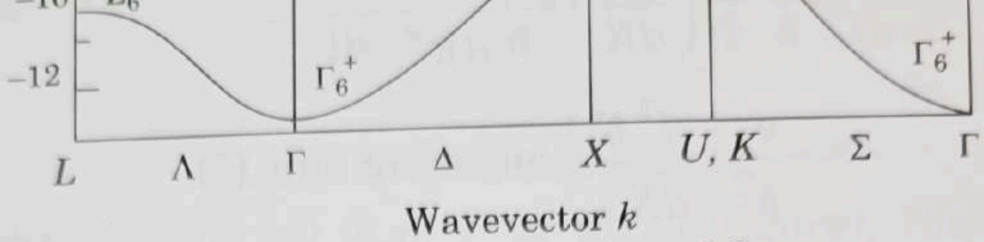


Fig. 2.15b. Band structure of Ge

2.5. EFFECTIVE MASS

In a crystal, electrons are not completely free, instead they interact with the periodic potential of the lattice. Thus while applying equations of electrodynamics to the charge carriers in a solid, we have to use altered values of particle masses. This is done to account for the influence of the lattice on charge carriers. By using their altered masses, electrons and holes can be treated as almost free carriers in most of the computations.

Let us consider an electron with wave vector K in the region where external electric field ε is present. It's particle velocity v will be equal to the group velocity $d\omega / dK$ *i.e.*,

$$v = \frac{d\omega}{dK} \quad \text{...(1)}$$

If ω be the angular frequency of the electron waves (*i.e.*, de broglie waves associated with electron), then its energy

$$E = \hbar\omega \quad \text{...(2)}$$

From equations (1) and (2),

$$v = \frac{1}{\hbar} \frac{dE}{dK} \quad \text{...(3)}$$

We consider the hypothetical case in which there is only one electron in the brillouin zone under consideration. Then in a time interval dt, electron energy increases by

$$dE = \text{work done by the electric force} = (-e\varepsilon)\,dx = -e\varepsilon\, v\, dt \qquad \text{...(4)}$$

where dx is the displacement of the electron during time dt. From equations (3) and (4)

$$dE = -\frac{e\varepsilon}{\hbar}\left(\frac{dE}{dK}\right)dt$$

Therefore

$$\hbar\frac{dK}{dt} = \frac{d(\hbar K)}{dt} = \frac{dp}{dt} = -e\varepsilon \qquad \text{...(5)}$$

where $p = \hbar K$ is the crystal momentum. Equation (5) is analogous to Newton's law of motion for the electron in a periodic lattice.

On differentiating eqn (3), we get

$$\frac{dv}{dt} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dK}\right) = \frac{1}{\hbar}\frac{d^2E}{dK^2}\frac{dK}{dt}$$

$$= -\frac{e\varepsilon}{\hbar^2}\left(\frac{d^2E}{dK^2}\right) \text{ on using eqn (5)}$$

or

$$-e\varepsilon = \left[\frac{\hbar^2}{(d^2E/dK^2)}\right]\frac{dv}{dt} \qquad \text{...(6)}$$

This equation is of the type

Force = mass × acceleration

Thus the quantity within square bracket in eqn. (6) may be regarded as the mass. It is known as the **effective mass** of the electron and is denoted by m^*. Hence

$$m^* = \frac{\hbar^2}{d^2E/dK^2} \qquad \text{...(7)}$$

represents the effective mass of an electron in a band with a given (E, K) relationship. Here d^2E/dK^2 represents the **curvature of the band**. Hence the curvature of the band determines the electron effective mass. The shape of the energy bands in three dimensional K-space determines the value of effective mass. The electron effective mass will be smaller in strongly curved bands (*e.g.*, Γ) and larger in those bands which have small curvature (*e.g.*, L or X).

The band structure of GaAs is shown in fig. 2.16. The binary compound GaAs is a direct band gap material with a band gap of 1.43 eV at room temperature. It has direct (at $K = 0$) conduction band minimum Γ alongwith two higher-lying indirect minima L and X in its conduction band.

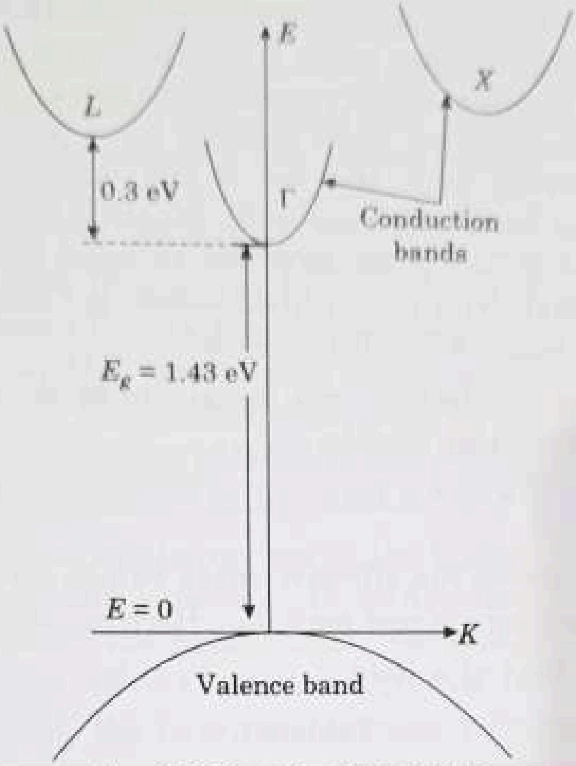


Fig. 2.16. Band structure of GaAs

For a band centered at $K = 0$ (*e.g.*, Γ in above figure), the (E, K) dispersion relation near the minimum is usually parabolic given by

$$E = \frac{\hbar^2 K^2}{2m^*} + E_g \qquad \text{...(8)}$$

In this case, the effective mass m^* turns out to be a constant. Similarly, for a free electron,

$$E = \frac{\hbar^2 K^2}{2m}$$

$$\therefore \quad \frac{d^2 E}{dK^2} = \frac{\hbar^2}{m}$$

$$\therefore \quad m^* = \frac{\hbar^2}{(d^2 E / dK^2)} = m$$

Thus for a free electron, the effective mass is equal to its actual mass. However for an electron moving in a periodic potential, the effective mass is different from actual mass of the electron *i.e.*,

$$m^* \neq m$$

In this case m^* varies with energy E or wavevector K. The electron behaves like a particle with variable effective mass. Thus effect of periodic potentials means replacement of m by m^*.

In many conduction bands the (E,K) relationship is not parabolic, rather they have complex dispersion relations which depend on the direction of electron transport with respect to the principal crystal directions. In such cases, the effective mass is a **tensor quantity.** Further in fig. 2.16., the curvature d^2E/dK^2 is positive at the conduction band minima, but is negative at the valence band maxima. Thus the electrons near the conduction band minima have positive values of effective mass whereas the electrons near the top of the valence band have **negative effective mass.** Valence band electrons with negative charge and negative mass move in an electric field in the same direction as holes with positive charge and positive mass. For materials with nearly filled bands, m^* will be negative. For holes near the top of valence band, m^* will be negative.

The effective mass of an electron in a metal can be determined from cyclotron resonance experiment. For most metals,

$$\frac{m}{2} \le m^* \le 2m$$

The following table shows the effective mass values for semiconductors Ge, Si and GaAs in terms of the electron rest mass m_0. Here m_n^* denotes the effective mass of electron whereas m_p^* that of a hole.

Table 2.1.

	Ge	Si	GaAs
m_n^*	$0.55\ m_0$	$1.1\ m_0$	$0.067\ m_0$
m_p^*	$0.37\ m_0$	$0.56\ m_0$	$0.48\ m_0$

2.6. FERMI SURFACES

In a solid, at very low temperatures the energy bands are filled with electrons upto a certain level, called the **Fermi level.** The energy corresponding to this level is called the **fermi energy E_F.** All levels with $E > E_F$ are empty. In three dimensional K-space the set of values of K_x, K_y and K_z which satisfy the equation $\hbar^2(K_x^2 + K_y^2 + K_z^2)/2m = E_F$, form a surface called the **fermi surface.** All (K_x, K_y, K_z) energy states that lie below this surface are full, and those above this surface are empty. The fermi surface encloses within it all the electrons in the conduction band that carry electric current. Thus we can say that **fermi surface of any metal is the surface of constant energy E_F** in the momentum (or K-) space. At absolute zero of temperature, it separates the unfilled quantum states from the filled ones. *The shape of the fermi surface plays an active role for determining electrical properties of metals.*

The fermi surface of a good conductor such as copper (electron density $n = 8.5 \times 10^{22}$) or silver (electron density $n = 5.86 \times 10^{22}$) can fill the entire brillouin zone. In the undoped (i.e. intrinsic) temperatures also. Thus **doping) concentration at room temperature.** For example, intrinsic silicon at $T = 300$ K has electron mobility $\mu_n = 1350$ cm^2/V-sec which decreases to just 700 cm^2/V-sec when silicon is doped with 10^{17} donor atoms per cm^3.

2.10. EXCITONS

An electron and a hole may be bound together through their mutual attractive electrostatic (*i.e.*, coulombic) interaction. **The bound electron-hole pair is called an exciton.** It is electrically neutral. It is an analog of positronium atom in a solid such as a semiconductor. Some excitons are intrinsically unstable with respect to decays into a free electron and free hole. All excitons are unstable against the ultimate recombination process in which the electron drops into the hole.

The positronium atom is the bound state of an electron and a positron under the attractive coulomb force. Its energy levels are given by

$$E = -\frac{q^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{6.8}{n^2}\ \text{eV} \qquad \ldots(1)$$

where,

$$a_0 = \text{Bohr radius} = \frac{4\pi\epsilon_0 \hbar^2}{m_0 q^2} = 0.0529\,\text{nm}$$

m_0 = free electron (and positron) mass $= 9.1 \times 10^{-31}$ kg

q = charge on an electron

n = principal quantum number $= 1, 2, 3, \ldots \infty$.

For ground state ($n = 1$), the energy of positronium atom is just -6.8 eV which is half of the ground state energy of the hydrogen atom. This is because the effective mass of positronium is half of that of the bound electron-proton pair in hydrogen atom.

In a semiconductor the electron is in the conduction band, and the hole is in the valence band. The effective mass of electron (m_e) and hole (m_h) are less than the mass (m_0) of a free electron. The effective mass of an exciton (bound electron-hole pair)

$$m^* = \frac{m_e . m_h}{m_e + m_h} = \frac{m_e}{1+(m_e / m_h)} \quad ...(2)$$

If $m_e << m_h$, then effective mass of exciton m^* becomes comparable with the electron effective mass. For example, if $m_e / m_h = 0.2$, then $m^* = 0.83\ m_e$. This is the case with GaAs. Also for these materials $7.2 < \in / \in_0 < 17.7$ where $\in_0$ is dielectric constant of free space and $\in / \in_0$ is relative dielectric constant. Thus these two factors decrease the exciton energy E' relative to the energy of positronium atom. Exciton energy levels are therefore given by

$$E' = \frac{(m^* / m_0)}{(\in / \in_0)^2} \frac{q^2}{4\pi \in_0 a_0 n^2} = \frac{13.6(m^* / m_0)}{(\in / \in_0)^2\, n^2} \text{eV} \quad ...(3)$$

These two factors (*i.e.*, effective mass and relative dielectric constant) also increase the effective Bohr radius of the electron orbit, which is expressed as

$$a_{exci} = \frac{\in / \in_0}{m^* / m_0} a_0 = \frac{0.0529}{m^* / m_0} \text{ nm} \quad ...(4)$$

For GaAs, $m^* / m_0 = 0.059$ and using the relative dielectric constant for GaAs, we get

$$E_0' = 4.6 \text{ MeV}$$

and

$$a_{exci} = 11.8 \text{ nm}$$

where E_0' is the ground state energy of exciton in GaAs. The effective Bohr radius of exciton (= 11.8nm) suggests that an exciton extends over quite a few atoms of the lattice. Its radius in GaAs is comparable with the dimensions of a typical nanostructure. An exciton exhibits characteristic optical spectra.

2.11. TYPES OF EXCITON

Two limiting categories of excitons are as follows :

I. Mott-Wannier Exciton : This is the **weakly bound exciton** as the one discussed above. The average electron-hole separation is large in comparison with a lattice constant. Its energy levels are similar to positronium atom as shown in fig. 2.23, though respective levels have lower energy values compared to positronium. Exciton levels lie in the forbidden gap. Excitons may be produced when photons of energy lower than the band gap energy, E_g, are absorbed by the crystal. *Almost all the excitons encountered in semiconductors and in nanostructures are of the Mott-Wannier type.*

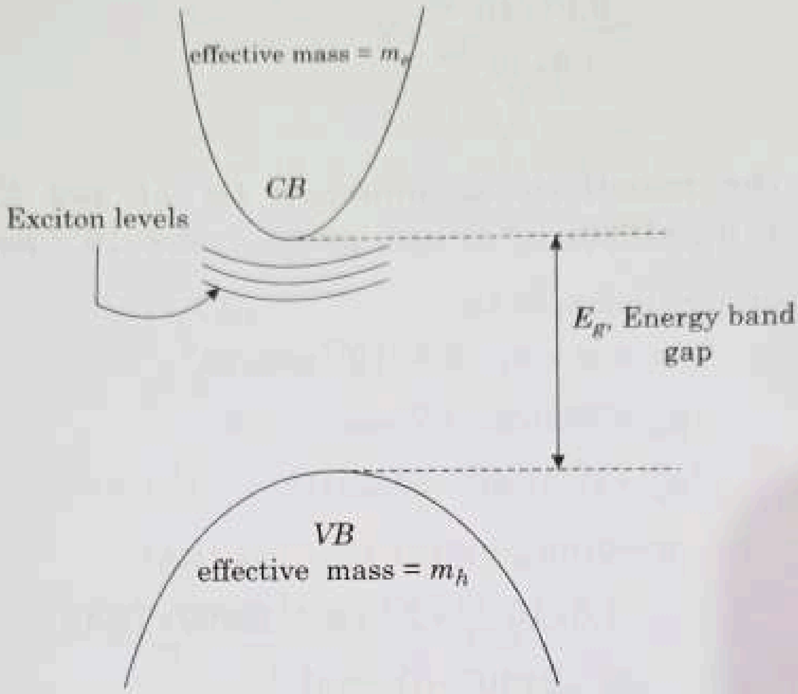


Fig. 2.23.

II. Frenkel Exciton : A **strongly or tightly bound exciton**, called a Frenkel exciton, is similar to a long-lived excited state of an atom or a molecule. It is small in size and is localized on any atom in the crystal. An ideal Frenkel exciton will travel as a wave throughout the crystal, but the electron is always close to the hole. The excitation wave of an exciton travels through the crystal just as the reversed spin of a magnon travels through the crystal.

Solved Examples

Ex. 1. ***Calculate the fermi energy when it is given that :***

$$\frac{N}{L} = 0.8 \textit{ electrons per } \text{Å}, \ h = 6.6\times10^{-34} \ Js, \ m_e = 9.1\times10^{-31} \ kg.$$

Sol. The fermi energy in one dimensional case is given by

$$E_F = \frac{h^2}{2m}\left(\frac{N}{4L}\right)^2$$

Substituting various values, we get

$$E_F = \frac{(6.6\times10^{-34})^2}{2\times9.1\times10^{-31}}\left(\frac{1}{4}\times\frac{0.8}{10^{-10}}\right)^2 \qquad \because \ 1\text{Å} = 10^{-10}\,\text{m}$$

$$= 0.0957\times10^{-17} \ J$$

$$= 9.57\times10^{-19} \ J$$

3.2. CLASSIFICATION OF LOW DIMENSIONAL MATERIALS

Bulk Material : It is a **three dimensional structure** in which there is no confinement along any direction. All of its dimensions are larger than the exciton Bohr radius. The particle is free to move throughout the volume of the material. No quantization of the particle motion occurs *i.e.*, particle have a continuous range of energies between a minimum and maximum.

Low dimensional structures are classified on the basis of number of reduced dimensions they possess. Dimensionality refers to the number of degrees of freedom possessed by the particle. The low dimensional structures, on the basis of dimensionality , are of the following types :

1. **Quantum Well :** It is a **two-dimensional nanostructure** in which there is confinement along one direction and particle is free to move in other two directions (*i.e.*, in a plane). Particle possess discrete (or quantized) energies associated with the confinement dimension. Particle energies are continuous along the other two (unconfined) dimensions.

2. **Quantum Wire :** It is a **one dimensional nanostructure** in which there is confinement along two directions and particle is free to move in the third direction. Particle has discrete energies associated with these two directions of confinement and continuous along the third (unconfined) direction.

3. **Quantum Dot :** The extreme case in which confinement of the particle occurs in all the three directions, results in a **zero-dimensional nanostructure**, called quantum dot. In this case, the number of degrees of freedom of the particle is zero. Particle has discrete energies associated with its motion along all the three directions. Examples of zero dimensional objects are-nanoparticles, clusters, colloids, nanocrystals, and fullerenes. Quantum dots are composed of several to a few thousand atoms.

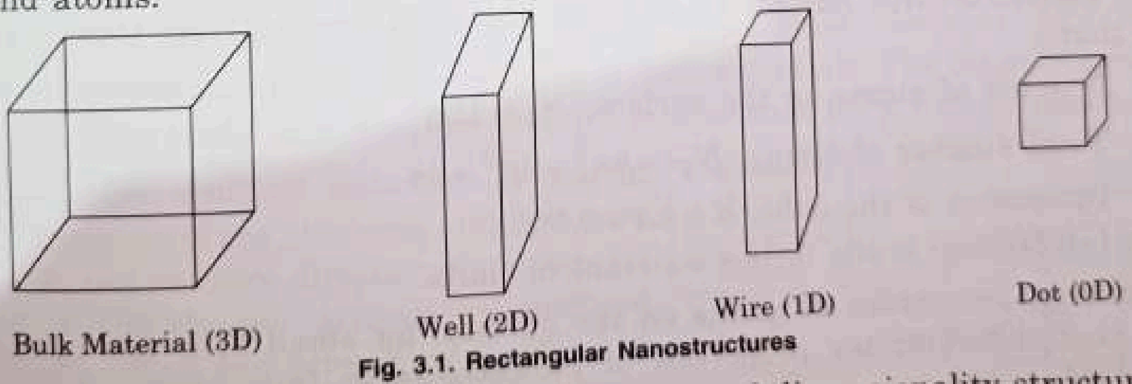


Fig. 3.1. Rectangular Nanostructures

From above discussion it is obvious that reduced dimensionality structures are labeled according to the remaining degrees of freedom in the particle motion, rather than by the number of confinement directions.

3.3. QUANTUM SIZE EFFECTS

The properties of a material are characterized by a specific **'length scale'** usually on the nanometer dimension. If the physical size of the material is reduced semiconductor. Quantum structures such as quantum wells, quantum wires or quantum dots are characterized with very small concentration of electrons. A higher doping level is required to have any significant electron concentration if size of the nanostructure is reduced below the electron de Broglie wavelength.

Imp

3.4. QUANTUM CONFINEMENT

In small nanocrystals (*i.e.*, nanomaterials), the electronic energy levels are not continuous as in the bulk but are discrete (shown by the existence of finite density of states), because of the confinement of the electronic wave function to the physical dimensions of the particles. This phenomena is called quantum confinement and therefore nanocrystals are also referred to as quantum dots. For a semiconductor particle, quantum confinement occurs when the nanocrystal radius becomes comparable to the exciton Bohr radius. The **confinement leads to a transition from continuous to discrete energy levels.** When materials are so small that they lie in the quantum confinement regime, then their electronic and optical properties deviate substantially from those of bulk materials. The discrete structure of energy states leads to a discrete absorption spectrum for a nanostructure.

A quantum confined structure is one in which the motion of the electrons and holes are confined in one or more directions by potential barriers. If the charge carriers are confined along one direction and delocalized (*i.e.* free) in the other two directions, then the resultant structure is a quantum well. When the confinement occurs in two dimensions and the carriers are delocalized in the remaining third dimension, then the resultant structure is a quantum wire or nanowire. A quantum dot may have shape of a tiny cube, a short

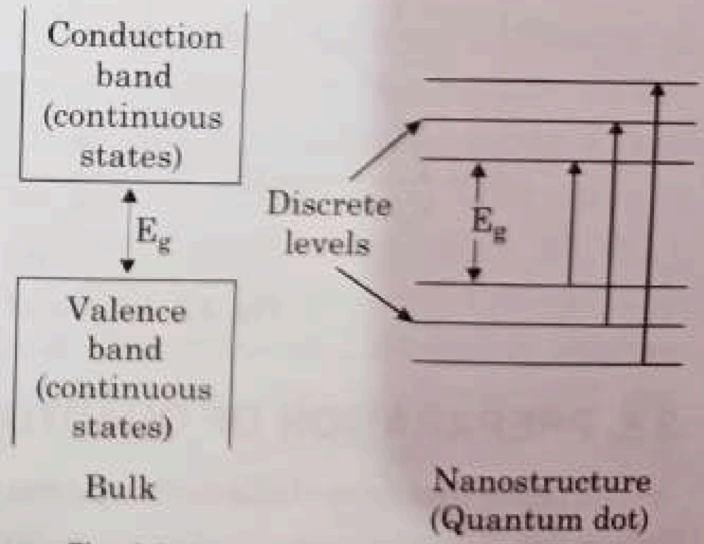


Fig. 3.2. Transition from continuous to discrete energy levels

cylinder, or a sphere with nanometer dimensions and exhibits confinement in all the three dimensions. There is no delocalization in this case. The following table summarizes the confinement and delocalization dimensions for various nanostructures.

Table. 3.1.

Quantum Structure	Confinement Dimensions	Delocalization (or free) Dimensions
Bulk conductor	0	3 (x, y, z, say)
Quantum Well/Superlattices	1 (z)	2 (x, y)
Quantum Wire	2 (x, y)	1 (z)
Quantum Dot/Nanocrystals	3 (x, y, z)	0

As more number of the dimensions is confined, more discrete energy levels can be found, *i.e.*, carrier movement is strongly confined in a given dimension.

Nanostructure		**Representation**
Quantum Well	⟷	Particle in 1D box
Quantum Wire	⟷	Particle in 2D box
Quantum Dot	⟷	Particle in 3D box

The density of states $D(E)$ determines the various electronic and other properties and as shown in Fig. 3.3, $D(E)$, differ dramatically for each of the three nanostructure types. Thus the nature of the dimensionality and of the confinement associated with a particular nanostructure have a noticeable effect on its properties.

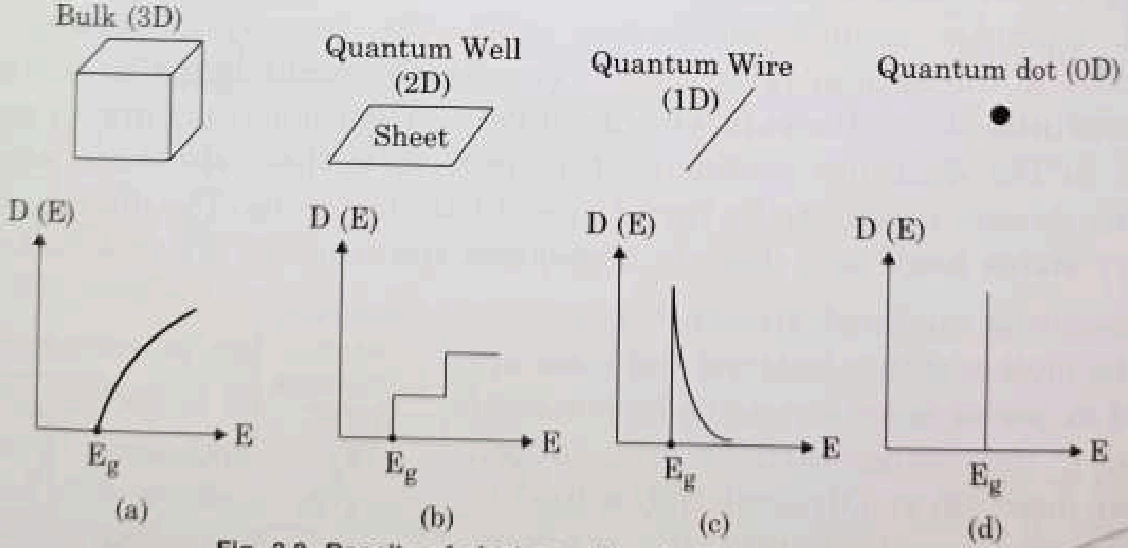


Fig. 3.3. Density of electron states for nanostructures

3.5. PREPARATION OF QUANTUM NANOSTRUCTURES

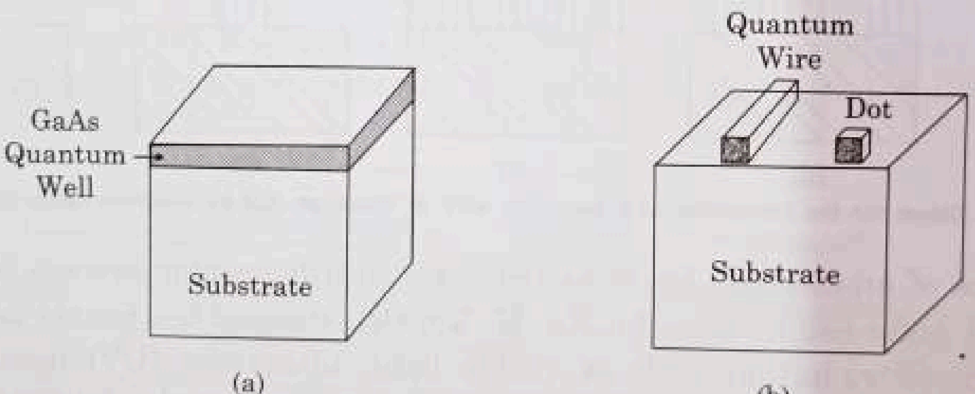
There are two different approaches of making quantum nanostructures :

I. Bottom-Up Methods : In the bottom-up approach, material and device are built from molecular components which assemble themselves chemically by

principles of molecular recognition. This is carried out by a sequence of chemical reactions which are controlled by catalysts. This bottom-up approach is **widespread in biology** where enzymes (working as catalysts) assemble amino acids to construct living tissues that forms and supports the organs of the body. It is based upon **self assembly of atoms or molecules** into a structure.

Bottom-up methods should be capable of producing devices in parallel (simultaneous production) and are therefore, cheaper than the top-down methods. There are many examples of self-assembly based on molecular recognition in biology, such as (i) Watson-Crick base pairing, and (ii) enzyme-substrate interactions.

II. Top-down Methods : This approach of preparing nanostructures starts with a large scale object or pattern and gradually reduces its dimension or dimensions without atomic level control. Top-down methods **use a technique called lithography.** In this technique, we shine radiation through a template onto a surface coated with a radiation-sensitive resist. The resist is then removed and the surface is chemically treated to produce nanostructure. A resist is a soft material. Polymethyl methacrylate $[C_5O_2H_8]_n$, a polymer, is a typical resist material. Fig. 3.4. shows the lithographic process of obtaining a quantum wire or quantum dot starting from a GaAs quantum well formed on a substrate.



(a) (b)

Fig. 3.4. Formation of Quantum wire or dot from a well

The whole lithographic process takes place in a number of steps as shown in Fig. 3.5. In the first step, a radiation sensitive resist is placed on the surface of the sample substrate (Fig. 3.5a). An electron beam (used as a radiation) is made to fall in the region where the nanostructure is to be placed (Fig. 3.5b). This can be achieved either by using mask that contains the nanostructure pattern or by a scanning electron beam that falls on the surface only in the desired region. The radiation chemically modifies the exposed region of the resist and makes it soluble in a developer. If the exposed material is etched away by the developer and the unexposed region is resilient, the material is called a positive resist. And if unexposed region is etched away by the developer, then resist is called a negative resist. In the next step (Fig. 3.5c), developer (e.g., tetramethylammonium hydroxide) is applied to remove the irradiated portions of the resist.

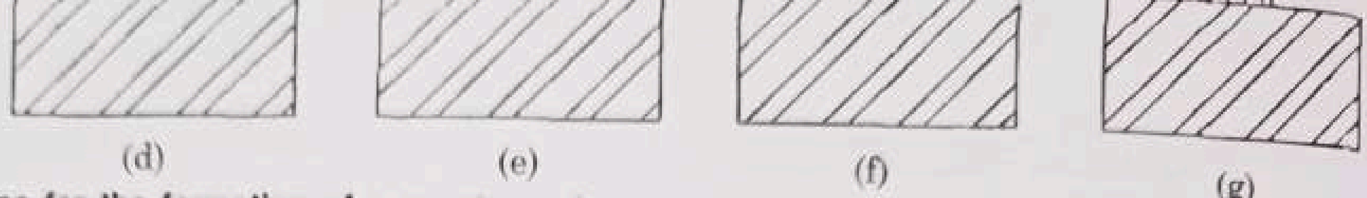

(d) (e) (f) (g)

Fig. 3.5. Steps for the formation of a quantum wire or quantum dot by electron-beam lithography

In place of an electron beam as radiation in lithographic process, we may also use neutral atom beams (*e.g.*, Li, Na, K, Rb, Cs); charged ion beams (*e.g.*, Ga^+); or electromagnetic radiation such as visible light, ultraviolet (UV) light, or X-rays. Laser beams as radiation source are suitable for quantum-dot fabrication.

3.6. FABRICATION OF QUANTUM DOT ARRAYS

Quantum dots are very small particles or nanocrystals of a semiconducting material with diameters in the range 2 to 10 nm and made of about 10 to 50 atoms. These are zero dimensional materials in which electrons are confined in 3-dimensions. *Quantum dot arrays are the collection of a large number of quantum dots fabricated simultaneously for specific applications.* These aggregates of quantum dots possess unique quantum properties and cooperative interactions useful for many technological applications. In this case, instead of starting with a single quantum well, the process starts with multiple quantum wells.

Let us consider a multiple (here four) quantum well structure as shown in Fig. 3.6. First of all a radiation sensitive resist is placed upon it, then a template or mask film is used with six circles cut out of it. Following all the steps explained in Fig. 3.5, we can produce a 24 quantum dot array, in which there are six columns, each containing 4 stacked quantum dots as shown in Fig. 3.7.

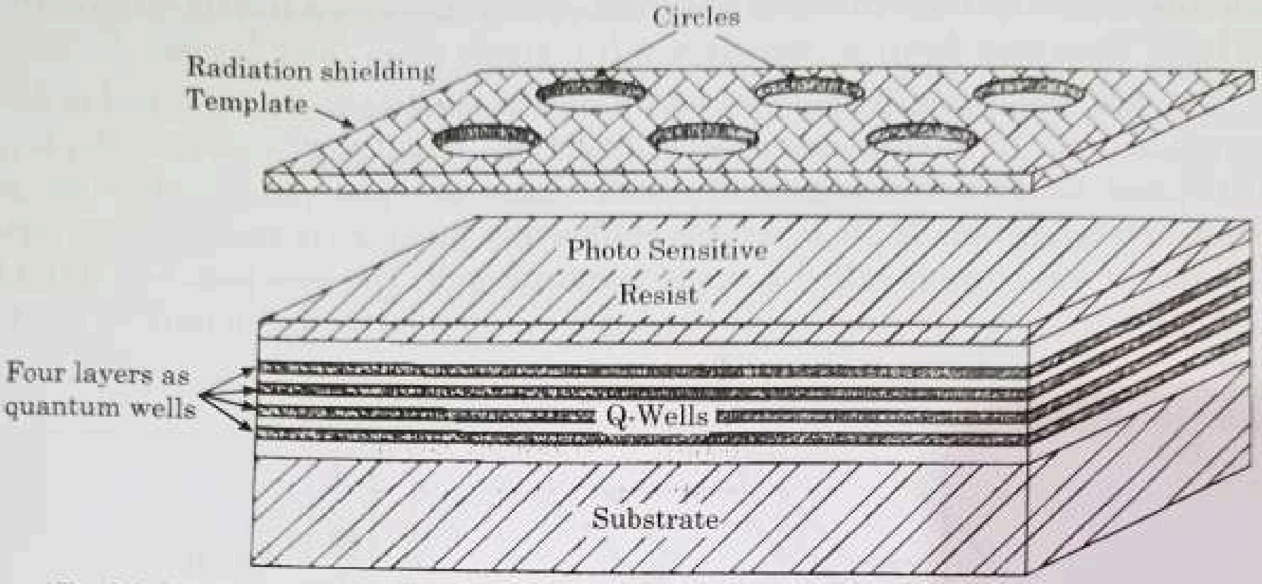


Fig. 3.6. Multiple-quantum-well arrangement mounted on a substrate and covered by a resist

The advantage of fabricating quantum dot arrays is that the **arrays produce a greatly enhanced photo-luminescent (PL) output of light.** Experiments have shown that a photo-luminescent spectrum from a quantum dot array is more than 100 times stronger than the spectrum obtained from the initial multiple quantum wells.

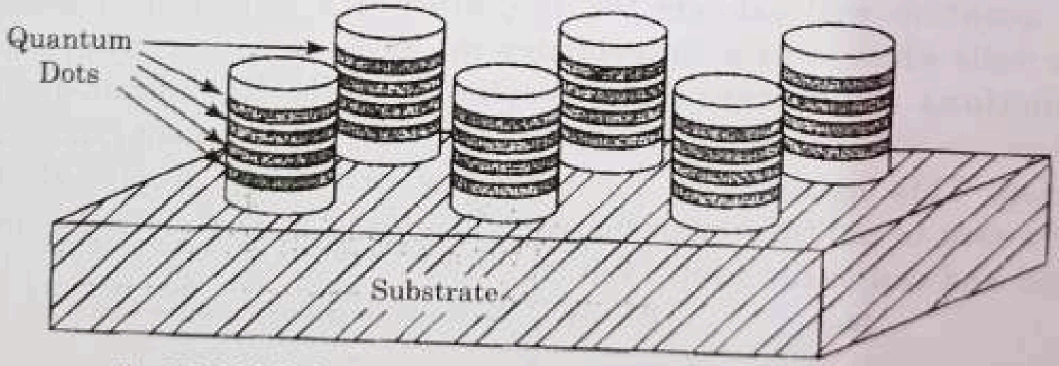


Fig. 3.7. 24-fold (or 6 × 4) quantum-dot array formed by lithography

3.7. QUANTUM WELL AND SUPERLATTICE

Idea of Quantum well structure

The term 'well' refers to a semiconductor region that is grown to possess a lower energy, so that it acts as a trap for electrons and holes. These wells are called quantum wells because such semiconductor regions are **only a few atomic layers thick**. Quantum wells are real-world implementation of the "particle in one-dimensional box" problem. They are experimentally realized by epitaxial growth of a sequence of ultrathin layers consisting of semiconducting materials of varying composition (*i.e.*, varying bandgap).

Quantum wells are formed in semiconductors by having a material like gallium arsenide (narrower band gap) sandwiched between two layers of a material with a wider band gap, like aluminium arsenide. These structures can be grown by molecular beam epitaxy (MBE) or chemical vapour deposition (CVD) with control of the layer thickness down to monolayers (*i.e.* single atom thick layers).

Two dissimilar semiconductors with different band gaps can be joined to form a heterojunction. If a thin layer of a narrower band gap material 'A' say, is sandwiched between two layers of a wider band gap material 'B', then we get a double heterojunction. If the layer A is sufficiently thin (*i.e.*, in the quantum regime) then such a structure is called a single quantum well. The quantum well formed by the heterojunction between a wide band gap semiconductor and a narrow band gap semiconductor is shown in Fig. 3.8.

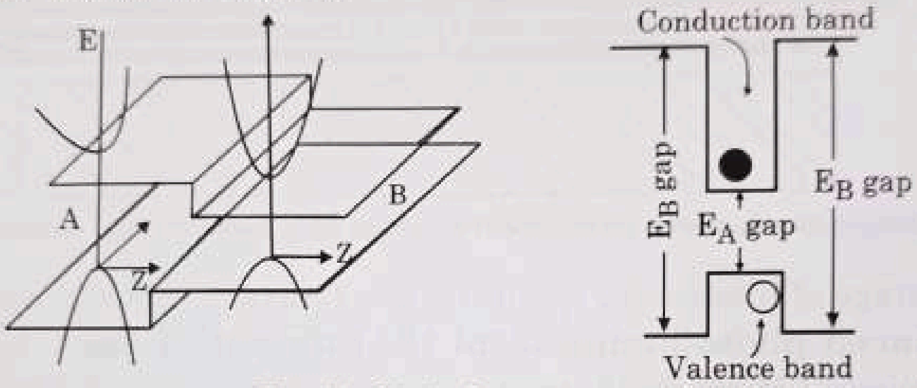
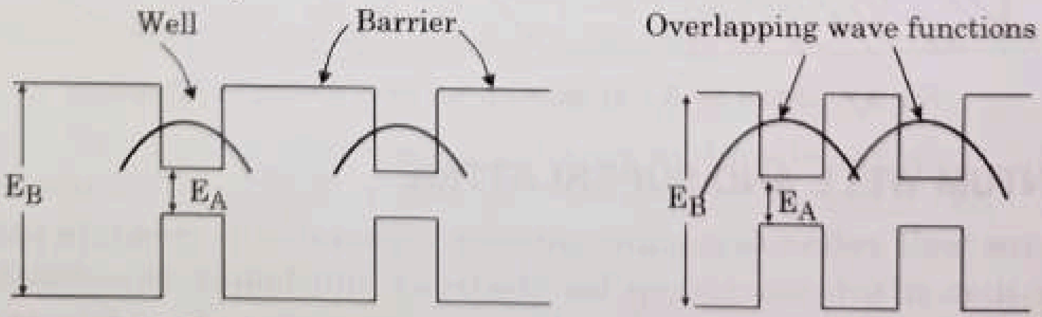


Fig. 3.8. Single Quantum Well

In the same manner we can form multiple quantum wells or superlattices. A multiple quantum well exhibits the properties of a collection of isolated single quantum wells whereas **in a superlattice** the barriers are very thin such that the **wave functions of adjacent wells overlap strongly**. In multiple quantum wells the barriers are wide enough such that wavefunctions in adjacent quantum wells do not overlap. This means that the tunneling probability from well to well is essentially zero in multiple quantum wells. However in superlattices electrons are delocalized and can easily tunnel out.



(a) Multiple Quantum Well

(b) Superlattice

Fig. 3.9

A superlattice can represent a lower dimensional structure such as an array of quantum dots or quantum wires. The periodic arrangement of quantum wells superimposes a different periodicity on top of the physical lattice, hence called a superlattice. This gives rise to the **formation of minibands within the superlattice.** It should be noted that the same structure can be a multiple quantum well at low temperature and superlattice at room temperature.

3.7.1. Application of Schroedinger Equation to Infinite Potential Well

Q.C. in 10.

Let us now discuss the problem of quantum confinement along one direction. It is same as the problem of particle in one dimensional box. In a quantum well (2D structure), particles are confined to a thin sheet of thickness 'a' along the x direction by infinite potential barriers, which create a quantum well as shown in fig. 3.10.

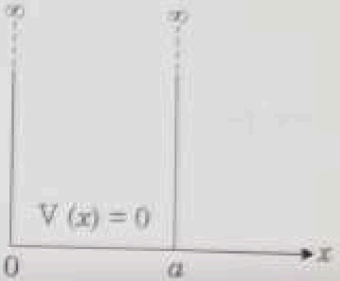


Fig. 3.10. Particle in infinitely deep potential well

In real systems, this confinement is due to electrostatic potentials (generated by external electrodes, doping, strain, impurities etc.); the presence of interfaces between different materials; the presence of surfaces; or a combination of these agents.

The potential function is

$$V(x) = \begin{cases} 0, & \text{for } \quad 0 < x < a \\ \infty, & \text{for } \quad x \le 0 \text{ or } x \ge a \end{cases} \quad \text{... (1)}$$

The Schroedinger equation in the potential well region where $V(x) = 0$, is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

or

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

or

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \text{... (2)}, \quad k^2 = \frac{2mE}{\hbar^2}.$$

The boundary conditions are

$$\psi(0) = \psi(a) = 0 \quad \text{... (3)}$$

The solution of equation (2) can be written as

$$\psi(x) = A\sin kx + B\cos kx \quad \text{... (4)}$$

Applying $\psi(0) = 0$, we get $B = 0$. So

$$\psi(x) = A\sin kx$$

Now $\psi(a) = 0$ gives, $A\sin ka = 0$

or

$$\sin ka = 0 = \sin n\pi \qquad \because \quad A \ne 0$$

or

$$ka = n\pi, \quad n = 1, 2, 3, \ldots$$

or

$$k = \frac{n\pi}{a}$$

Thus, the solution of eqn. (2) is

$$\psi(x) = A \sin \frac{n\pi}{a} x \qquad \text{... (5)}$$

Applying the normalization condition of wave function

$$\int_0^a \psi^* \psi \, dx = 1,$$

we get

$$A = \sqrt{\frac{2}{a}}$$

$$\therefore \quad \psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x \qquad \text{... (6)}$$

represents normalized eigen functions of the particle inside the well.

Also,

$$k^2 = \frac{2mE}{\hbar^2},$$

or

$$\frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

or

$$E_n = E = \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{n^2h^2}{8ma^2} \qquad \text{... (7)}$$

are the **discrete energy states of the particle within the quantum well region**. However, outside the well region particle energies are continuous. Here n is called the principal quantum number.

$$E_{(n+1)} - E_n = \frac{\{(n+1)^2 - n^2\}\pi^2\hbar^2}{2ma^2} = \frac{(2n+1)\pi^2\hbar^2}{2ma^2}$$

or

$$(E_{(n+1)} - E_n) \propto \frac{1}{a^2} \quad \text{and} \quad \propto (2n+1)$$

As the dimension $(= a)$ of the energy well increases, the spacing between discrete energy levels decreases. In the infinite crystal (i.e., bulk), a continuum occurs.

Above analysis shows that confinement of particle motion leads to discreteness or quantization of particle energies. The spacings between energy levels increases as principal quantum number n increases.

Zero Point Energy

The lowest energy (for $n = 1$) in the above case is

$$E_0 = \frac{\pi^2\hbar^2}{2ma^2} \neq 0$$

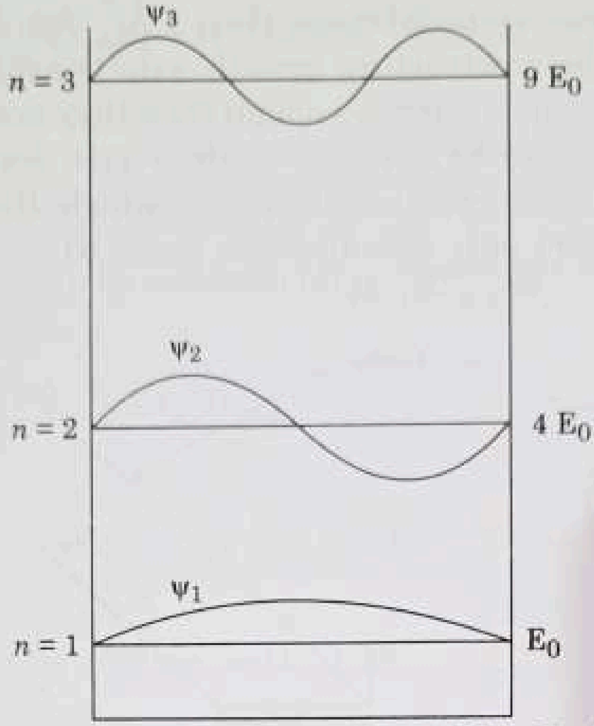


Fig. 3.11. First three eigen energies and eigen functions

This energy E_0 is called the zero-point energy or confinement energy. Its origin lies in the Heisenberg's uncertainty principle. Since the particle is constrained within a finite region, the variability in its position has an upper bound *i.e.* uncertainty in its position is finite whose maximum value can be 'a'. Therefore uncertainty in particle's momentum cannot be zero, the particle must contain some energy in this lowest state. The zero point energy increases with decrease in the width of the well.

3.8. QUANTUM WIRES

It is a one-dimensional nanostructure in which there is confinement along two dimensions and only one dimension is free for motion of charge carriers. A quantum wire or nanowire can be obtained from a quantum well by the process of lithography.

A standard quantum well layer can be fabricated by the process of photolithography or electron beam lithography and chemically etched to leave a free standing strip of quantum well material; the latter may or may not be filled in with

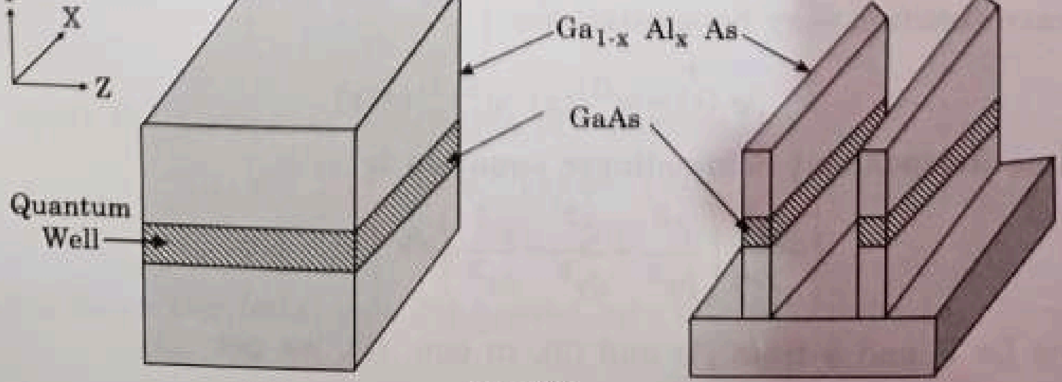


Fig. 3.12.

an overgrowth of the barrier material (here, $Ga_{1-x}Al_xAs$). Any charge carriers are still confined along the heterostructure growth axis (z-axis), as they were in the quantum well, but if the strip is narrow enough then they are also confined along an additional direction which may be either x – or the y-axis, depending on lithography. In the Fig. 3.13. a quantum wire is shown in which the electron (or hole) is delocalized (free) to move in only one direction (here, x).

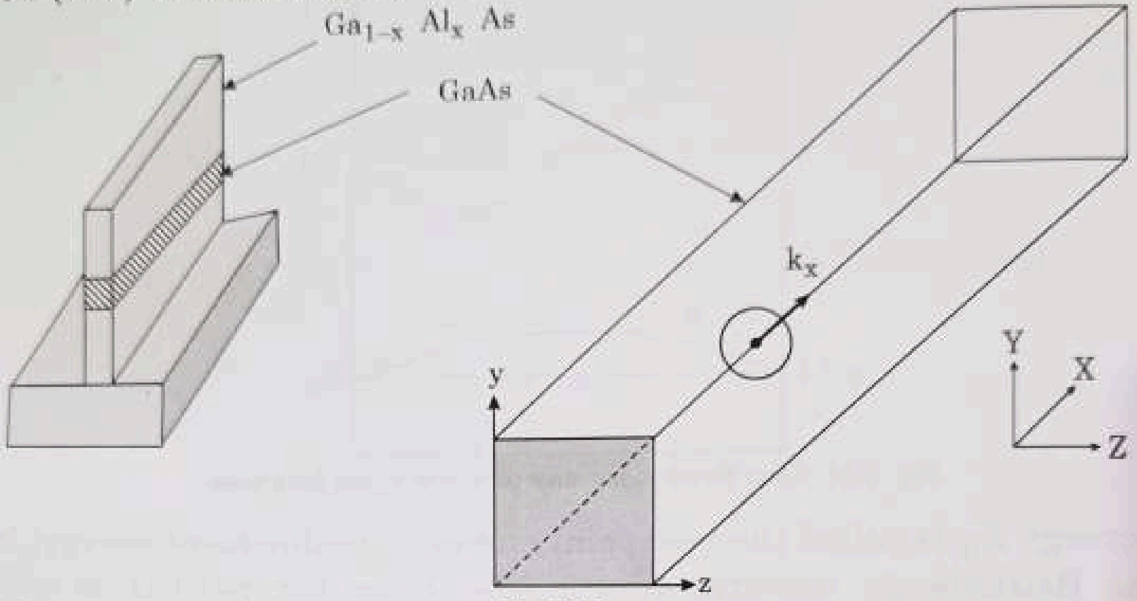


Fig. 3.13.

Ele$^{\ominus}$ confinement in 2D

3.8.1. Application of Schroedinger Equation to the Problem of Particle in 2D Box

The problem of a quantum wire is analogous to the particle in two dimensional box problem from the confinement point of view. Let us consider a two-dimensional box as shown in Fig. 3.14. Let confinement is along y- and z-directions and the motion of the charge carrier is free along x-direction.

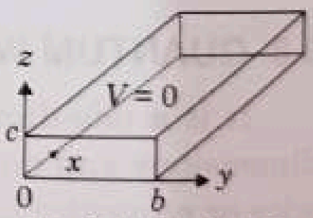


Fig. 3.14. Particle in 2D Box

The potential $V(\vec{r})$ is written as the sum of a two dimensional confinement potential (in the yz plane) plus a potential along the wire (*i.e.*, along x-axis) as

$$V(\vec{r}) = V^{(1)}(x) + V^{(2,3)}(y,z) \quad \text{... (1)}$$

The wave function may be written as

$$\psi(\vec{r}) = \psi^{(1)}(x)\ \psi^{(2,3)}(y,z) \quad \text{... (2)}$$

The time independent Schroedinger equation is

$$\left\{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V\right\}\psi = E\psi \quad \text{... (3)}$$

Putting for V and ψ from (1) and (2), in eqn. (3), we get

$$\left\{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V^{(1)}(x)+V^{(2,3)}(y,z)\right\}\psi^{(1)}(x)\,\psi^{(2,3)}(y,z)$$

$$=E\,\psi^{(1)}(x)\,\psi^{(2,3)}(y,z) \qquad \text{... (4)}$$

Writing $E = E^{(1)} + E^{(2,3)}$ and noting the fact that potential is zero everywhere inside the box (*i.e.*, $V^{(1)}(x) = 0$), equation (4) is equivalent to two equations which are as follows :

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(1)}(x)}{dx^2}=E^{(1)}\psi^{(1)}(x) \qquad \text{... (5a)}$$

and $-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi^{(2,3)}(y,z)+V^{(2,3)}(y,z)\,\psi^{(2,3)}(y,z)=E^{(2,3)}\psi^{(2,3)}(y,z)$ ... (5b)

Equation (5a) may be written in the form

$$\frac{d^2\psi'(x)}{dx^2} + \frac{2mE'}{\hbar^2}\psi'(x) = 0$$

$$\frac{d^2\psi^{(1)}(x)}{dx^2}+k_x^2\,\psi^{(1)}(x)=0, \quad \text{... (6)}, \qquad k_x^2=\frac{2mE^{(1)}}{\hbar^2}$$

It has plane wave solution given by

$$\psi^{(1)}(x)\approx\exp(i\,k_x\,x)$$

where k_x is the particle momentum along x-direction in which it is free to move with energy

$$E^{(1)}=\frac{\hbar^2 k_x^2}{2m} \qquad \text{... (7)}$$

Now to solve equation (5b), the potential $V^{(2,3)}(y,z)$ has the form

$$V^{(2,3)}(y,z)=\begin{cases}0 & \text{when } 0<y<b \text{ and } 0<z<c\\ \infty & \text{otherwise}\end{cases} \qquad \text{... (8)}$$

Outside the box, $\psi^{(2,3)}(y,z)=0$ because particle cannot be outside it. Thus, within the box, equation (5b) in the light of eqn. (8), reduces to

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi^{(2,3)}(y,z)=E^{(2,3)}\psi^{(2,3)}(y,z) \qquad \text{... (9)}$$

To apply the method of separation of variables, let

$$\psi^{(2,3)}(y,z)=\psi^{(2)}(y)\,\psi^{(3)}(z)$$

$$E^{(2,3)}=E^{(2)}+E^{(3)}$$

Using these two facts, eqn. (9) breaks into two equations as

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(2)}(y)}{dy^2} = E^{(2)}\psi^{(2)}(y) \Big/ \frac{d^2\psi^2(y)}{dy^2} + \frac{2mE^2}{\hbar^2}\psi^2(y) = 0 \quad \text{... (10a)}$$

and
$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(3)}(z)}{dz^2} = E^{(3)}\psi^{(3)}(z) \Big/ \frac{d^2\psi^3(z)}{dz^2} + \frac{2mE^3}{\hbar^2}\psi^3(z) = 0 \quad \text{... (10b)}$$

These equations may be written as

$$\frac{d^2\psi^2(y)}{dy^2} + k_y^2\psi^2(y) = 0 \quad \text{...(11a);} \quad k_y^2 = \frac{2mE^{(2)}}{\hbar^2}$$

and
$$\frac{d^2\psi^3(z)}{dz^2} + k_y^2\psi^3(z) = 0 \quad \text{...(11b);} \quad k_z^2 = \frac{2mE^{(3)}}{\hbar^2}$$

Both of these equations are similar to the Schrodinger equation in the infinitely deep potential well and have the same boundary conditions too. The standard boundary condition of the wavefunction being continuous at the walls of the box implies that the product of $\psi^{(2)}(y)$ and $\psi^{(3)}(z)$ must vanish at the walls. These boundary conditions when applied to (11a) and (11b) give normalized eigen functions as

$$\psi_{n_y}^{(2)}(y) = \sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi y}{b}\right);\ n_y = 1,2,3...$$

and
$$\psi_{n_z}^{(3)}(z) = \sqrt{\frac{2}{c}}\sin\left(\frac{n_z\pi z}{c}\right);\ n_z = 1,2,3...$$

Therefore,

$$\psi_{(n_y,\,n_z)}^{(2,\,3)} = \sqrt{\frac{4}{bc}}\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right) \quad \text{... (12)}$$

As is clear from (12), the quantum states in a quantum wire are described by two principal quantum numbers n_y and n_z. The energy levels of a quantum wire are given by

$$\left.\begin{aligned} E_{n_y} &= \frac{\pi^2\hbar^2 n_y^2}{2mb^2}, \quad n_y = 1,2,3,... \\ \text{and} \quad E_{n_z} &= \frac{\pi^2\hbar^2 n_z^2}{2mc^2}, \quad n_z = 1,2,3,... \end{aligned}\right\} \quad \text{... (13)}$$

The energy associated with particle motion in free direction (*i.e.*, *x*-) is

$$E(k_x) = \frac{\hbar^2 k_x^2}{2m} \quad \text{...(14)}$$

Thus, total energy of the particle in a quantum wire is given by

$$E_{(n_y,\, n_z)}(k_x) = \frac{\hbar^2 k_x^2}{2m} + \frac{\pi^2 \hbar^2 n_y^2}{2mb^2} + \frac{\pi^2 \hbar^2 n_z^2}{2mc^2} \qquad \text{...(15)}$$

Thus, the energy of the particle along the confinement directions (*y* and *z*) is discrete whereas it can have any value along unconfined (or free) direction (*i.e.*, along *x* -axis). Total energy of the particle in a quantum wire is not discrete. Further, the eigen energy in a quantum wire increases for decreasing size and a lower effective mass results in a larger eigen energy for a given size of the box.

The applications of nanowires are due to the fact that besides exhibiting quantum confinement effects, nanowire materials are at the same time in the shape of wires. So making electrical connections to the outside world and assembling actual devices may be a lot easier than with other nanostructures, such as quantum dots or quantum wells.

Crossed nanowire junctions have been made, using *p*-type and *n*-type nanowires. These may be used as diodes, or memory elements or as electro luminescent devices (LEDs or Solar Cells). Nanowires have also been used as sensors for monitoring changes in the conductance experienced when different compounds or gases are adsorbed to the surface of the nanowire. Thus, in future, nanowires may serve as efficient sensors for minute amounts of toxic gases, chemical weapons and explosives. v2.

3.9. QUANTUM DOTS

It is a zero dimensional nano-structure in which there is confinement of the particle along all the three directions. The particle is not free to move in any direction. Quantum dots have their radii in the typical range of 2 to 10 nm. Quantum dots can be formed by lithography and etching if a quantum well sample is etched to leave pillars rather than wires as shown in Fig. 3.15.

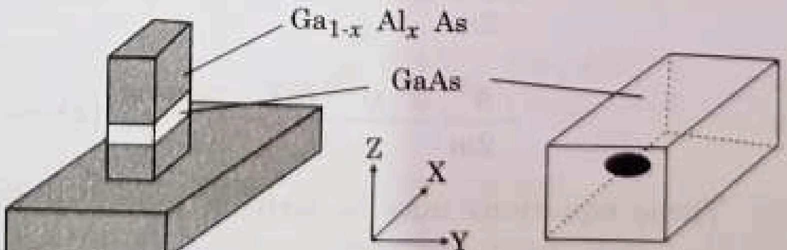
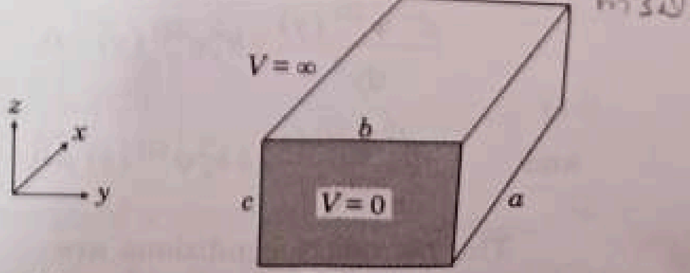


Fig. 3.15.

3.9.1. Application of Schroedinger Equation to a Particle in Quantum Box

cle° confinement in 3D.

Let us discuss the problem of quantum dot from confinement point of view. We consider a cuboid quantum dot or quantum box as shown in Fig. 3.16(b). Spherical quantum dots require numerical solution of Schroedinger equation. The quantum box is a generalization of a quantum wire of rectangular cross-section in which there is additional confinement along



(a) (b)

Fig. 3.16.

the x-direction such that $0< x< c$. Thus, the particle has no degrees of freedom in its momentum and it is now localized in all the three directions. Hence, it has discrete energy states associated with all the three directions of motion.

Let the potential be zero inside the quantum box but infinite everywhere else i.e.,

$$V(x,y,z)=\begin{cases}0 & \text{for } 0< x< a,\ 0< y< b \text{ and } 0< z< c\\ \infty & \text{otherwise}\end{cases} \quad \text{... (1)}$$

Three dimensional time independent Schroedinger equation within the box ($V=0$), is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)=E\psi(x,y,z) \quad \text{... (2)}$$

The wave function may be written as a product

$$\psi(x,y,z)=\psi^{(1)}(x)\psi^{(2)}(y)\psi^{(3)}(z) \quad \text{... (3)}$$

and the energy can be written as a sum

$$E=E^{(1)}+E^{(2)}+E^{(3)} \quad \text{... (4)}$$

where $E^{(1)}, E^{(2)}, E^{(3)}$ are particle energies along x, y and z directions respectively.

Using (3) and (4) in equation (2), which then separates into three equations as

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(1)}(x)}{dx^2}=E^{(1)}\psi^{(1)}(x) \quad \text{... (5a)}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(2)}(y)}{dy^2}=E^{(2)}\psi^{(2)}(y) \quad \text{.. (5b)}$$

or

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(3)}(z)}{dz^2}=E^{(3)}\psi^{(3)}(z) \quad \text{... (5c)}$$

These equations may be written in simple form as

$$\frac{d^2\psi^{(1)}(x)}{dx^2}+k_x^2\psi^{(1)}(x)=0, \qquad k_x^2=\frac{2mE^{(1)}}{\hbar^2} \quad \text{... (6a)}$$

$$\frac{d^2\psi^{(2)}(y)}{dy^2}+k_y^2\psi^{(2)}(y)=0, \qquad k_y^2=\frac{2mE^{(2)}}{\hbar^2} \quad \text{... (6b)}$$

and

$$\frac{d^2\psi^{(3)}(z)}{dz^2}+k_z^2\psi^{(3)}(z)=0, \qquad k_z^2=\frac{2mE^{(3)}}{\hbar^2} \quad \text{... (6c)}$$

The boundary conditions are

$$\psi^{(1)}(x) = 0 \quad \text{at} \quad x = 0 \text{ and } x = a$$

$$\psi^{(2)}(y) = 0 \quad \text{at} \quad y = 0 \text{ and } y = b$$

$$\psi^{(3)}(z) = 0 \quad \text{at} \quad z = 0 \text{ and } z = c$$

The normalized plane wave solutions of above equations on using boundary conditions of continuity of wave functions at the walls of the box, are

$$\psi_{n_x}^{(1)}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \quad \text{... (7a)}$$

$$\psi_{n_y}^{(2)}(y) = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \quad \text{... (7b)}$$

and

$$\psi_{n_z}^{(3)}(z) = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right) \quad \text{... (7c)}$$

The eigen energies are given by

$$E_{n_x}^{(1)} = \frac{\hbar^2 k_x^2}{2m} = \frac{\pi^2 \hbar^2 n_x^2}{2ma^2} \quad \text{...(8a)}, \quad k_x = \frac{n_x \pi}{a}$$

$$E_{n_y}^{(2)} = \frac{\hbar^2 k_y^2}{2m} = \frac{\pi^2 \hbar^2 n_y^2}{2mb^2} \quad \text{...(8b)}, \quad k_y = \frac{n_y \pi}{b}$$

$$E_{n_z}^{(3)} = \frac{\hbar^2 k_z^2}{2m} = \frac{\pi^2 \hbar^2 n_z^2}{2mc^2} \quad \text{...(8c)} \quad k_z = \frac{n_z \pi}{c}$$

Thus, the complete eigen functions of a quantum dot or a particle in quantum box are

$$\psi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \quad \text{... (9)}$$

which involves three principal quantum numbers whose values are

$$n_x = 1, 2, 3, \ldots; \; n_y = 1, 2, 3, \ldots; \; n_z = 1, 2, 3, \ldots .$$

Also the eigen energy corresponding to an eigen function is given by

$$E_{n_x, n_y, n_z} = E_{n_x}^{(1)} + E_{n_y}^{(2)} + E_{n_z}^{(3)}$$

or

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \quad \text{... (10)}$$

As is clear from equation (10), the total energy of a quantum dot, E_{n_x, n_y, n_z}, is discrete depending upon three quantum numbers n_x, n_y, n_z. The striking difference between the case of a quantum dot and that of a quantum well or wire is that in this case **total energy is quantized** whereas in the well or wire case only the energy associated with the directions of confinement is quantized. This quantization feature is typical of atoms, therefore **quantum dots or quantum boxes are sometimes referred to as artificial atoms.**

A remarkable feature of a quantum box is that when two or more of the dimensions are the same (*e.g.*, $a = b$), more than one eigenfunction corresponds to the same total energy. Such eigen values are called **degenerate eigen values** and the number of eigen functions corresponding to it is called degeneracy of that energy level. Degeneracy results from the symmetry of the structure.

Quantum dots have following applications :

1. Quantum dots, particularly CdSe, have narrow emission spectra and since different sized dots emit different colours, therefore these dots may be used for biological labeling. Dots are much more resistant to fading. However, labeling of proteins or cells or other biological specimen, is done with the help of organic dyes not with quantum dots.

2. Colloidal CdSe quantum dots may be used in efficient multicolour lasers.

3. Since quantum dots have tunable, size dependent absorption and emission spectra, therefore they may be used in fabricating efficient solar cells which can operate even under cloudy conditions and on rainy days.

4. Since different sized quantum dots emit different colours, therefore quantum dots may be used in making light emitting devices (LEDs).

5. Quantum dots may be used as conducting islands in single electron transistors (SETs) due to confinement effects. Quantum dots may be used to store charge and hence can be used in a memory device.

3.10. PARTICLE IN AN INFINITE CIRCULAR BOX : TWO DIMENSIONS OF CONFINEMENT

This case of confinement is concerned with a quantum wire of circular cross-section. Let the particle is confined to a circular cross-section of the wire with radius 'a'. The particle is free to move along the length of the wire. The potential in this case is represented by

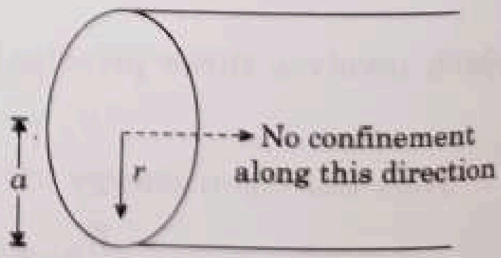


Fig. 3.17.

$$V(r) = \begin{cases} 0 & \text{if} \quad r < a \\ \infty & \text{if} \quad r \geq a \end{cases} \qquad \ldots (1)$$

The time independent Schroedinger equation relevant to this case is

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

4.1. INTRODUCTION

Density of states (DOS) is defined as the number of different states at a given energy level that electrons are allowed to occupy. The DOS is a measure of how close together the energy levels are to each other. In three dimensional structures it is equal to the number of electron states per unit volume per unit energy interval. It is represented by $g(E)$. If dN be the number of available electron states per unit volume at energy E in the energy interval E to $E + dE$, then density of states is defined as :

$$g(E) = \frac{dN(E)}{dE} \qquad \text{... (1)}$$

The calculation of some electronic processes like absorption, emission, and the general distribution of electrons in a material requires the knowledge of the number of available states per unit volume per unit energy range *i.e.,* the density of states, **Bulk properties such as specific heat, paramagnetic suceptibility, and other transport phenomena of conductive solids depend on density of states function**. The behaviour of density of states function with respect to the energy depends upon the dimensionality of the system (material). The density of states function provides useful information about the electronic structure of 3D (bulk), 2D (quantum well), 1D (quantum wire) and 0D (quantum dot) materials. The density of states can be used to determine the spacing between energy bands in semiconductors. In this chapter we will derive expressions for density of states for materials of different dimensions.

4.2. DENSITY OF STATES IN THREE DIMENSIONS (BULK)

Let us first calculate the density of states for a bulk (3D) material in which there is no confinement at all. Thus, there are three degrees of freedom and the electrons are free to move along all the three (x, y, z) directions. The energy E is related to the propagation constant k (magnitude of wave vector) as

$$E = \frac{\hbar^2 k^2}{2m} \qquad \text{... (1)}$$

Consider the volume in reciprocal space (*i.e.*, k space)

$$V_k = \frac{4}{3}\pi k^3$$

where
$$k^2 = k_x^2 + k_y^2 + k_z^2$$

and
$$k_x = \frac{2\pi}{L_x}, \quad k_y = \frac{2\pi}{L_y}, \quad k_z = \frac{2\pi}{L_z}.$$

Here L_x, L_y, L_z are the length of the material along x, y, z directions. The factor of 2π occurs due to the application of periodic boundary conditions on the material. A set of (k_x, k_y, k_z) values represents a mode. Thus

Volume occupied by each mode $= k_x \,.\, k_y \,.\, k_z$

$$= \frac{(2\pi)^3}{L_x\, L_y\, L_z}$$

Therefore the number of modes in the spherical volume V_k are given by

$$= \frac{\text{Volume of sphere}}{\text{Volume of each mode}} = \frac{V_k}{k_x\, k_y\, k_z} = \frac{\frac{4}{3}\pi k^3}{(2\pi)^3 / L_x\, L_y\, L_z}$$

For electrons, there are two states (spin up and spin down) with same energy, then the number of electron states (or modes) in the volume V_k are

$$= 2 \times \frac{\frac{4}{3}\pi k^3}{(2\pi)^3 / L_x\, L_y\, L_z}$$

$$= \frac{k^3}{3\pi^2} L_x\, L_y\, L_z \qquad \text{... (2)}$$

The number of electron states per unit volume of the material

$$N = \frac{\text{Total number of states}}{\text{Volume of the specimen}} = \frac{\frac{k^3}{3\pi^2} L_x\, L_y\, L_z}{L_x\, L_y\, L_z}$$

$$N = \frac{k^3}{3\pi^2} \qquad \text{... (3)}$$

$\therefore$ Density of states

$$g(E) = \frac{dN}{dE} = \frac{d\left(\frac{k^3}{3\pi^2}\right)}{dE}$$

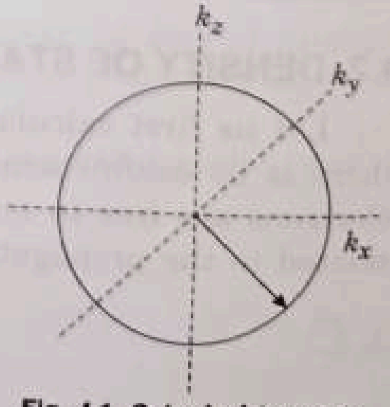


Fig. 4.1. Spherical *k*-space

$$= \frac{1}{3\pi^2}\,\frac{3k^2\,dk}{dE} = \frac{k^2}{\pi^2}\left(\frac{dk}{dE}\right) \qquad \text{... (4)}$$

From equation (1),

$$k^2 = \frac{2mE}{\hbar^2} \text{ or } k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\therefore \qquad dk = \sqrt{\frac{2m}{\hbar^2}}\,\frac{1}{2}E^{-1/2}\,dE$$

Putting these values in equation (4), we get

$$g(E) = \frac{1}{\pi^2} \times \frac{2mE}{\hbar^2} \times \sqrt{\frac{2m}{\hbar^2}}\,\frac{1}{2}\,E^{-1/2}$$

or

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \qquad \text{... (5)}$$

This is the "density of states" in three dimensions. It is clear that

$$g(E)\ \alpha\ E^{1/2}$$

Thus density of states of a bulk three dimensional material is a parabolic function of its energy. Fig. 4.2. shows a plot of $g(E)$ versus E for a bulk three dimensional material. Clearly, **density of states in three dimensional system increases with increase in energy of the system.**

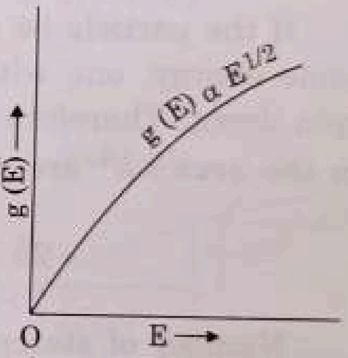


Fig. 4.2.

4.3. DENSITY OF STATES IN TWO DIMENSIONS (QUANTUM WELL)

In a two-dimensional material such as a quantum well, electron motion is confined along one direction (say, z) and they are free to move along rest of the two directions (x, y). Thus electron energy is quantized in one dimension. Total energy of this material is the sum of the energy along the quantized direction and the energy along the other two (*i.e.*, free) directions. It can be expressed as

$$E = \frac{\hbar^2 k_z^2}{2m} + \frac{\hbar^2 k^2}{2m} = E_n + E_{x,y} \qquad \text{... (1)}$$

where $k^2 = k_x^2 + k_y^2$ and $k_z = \frac{n\pi}{L_z}$. Here $n = 1, 2, 3, \ldots$ is an integer.

Let us now consider the circular area of k space

$$A_k = \pi k^2$$

Hence along x and y directions the particle is free to move, therefore due to periodic boundary conditions

$$k_x = \frac{2\pi}{L_x}$$

$$k_y = \frac{2\pi}{L_y}$$

Area of each mode $= k_x\,k_y = \dfrac{(2\pi)^2}{L_x\,L_y}$ ... (2)

Total number of modes in the area A_k is given by

$$= \frac{\text{Total area}}{\text{Area of each mode}} = \frac{\pi k^2}{(2\pi)^2/L_x\,L_y}$$

$$= \frac{k^2}{4\pi} L_x\,L_y \qquad \text{... (3)}$$

If the particle be an electron, then there can be two electrons corresponding to same energy, one with spin up and the other with spin down. Therefore total number of energy states in the area πk^2 are given by

$$= 2 \times \frac{k^2}{4\pi} L_x\,L_y = \frac{k^2}{2\pi} L_x\,L_y \qquad \text{... (4)}$$

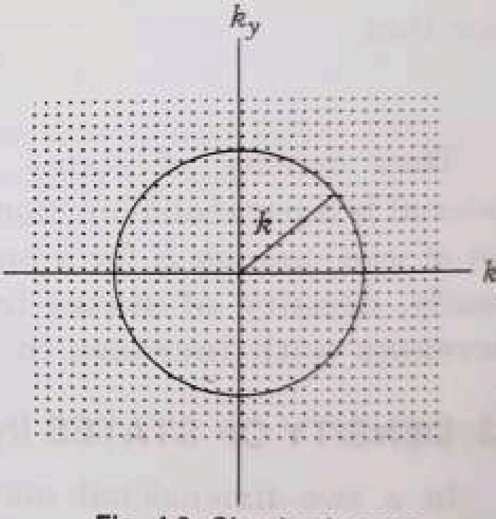


Fig. 4.3. Circular *k*-space

Number of states per unit area

$$N = \frac{\text{Total number of states}}{\text{Area}}$$

$$= \frac{\dfrac{k^2}{2\pi} L_x\,L_y}{L_x\,L_y}$$

$$= \frac{k^2}{2\pi} \qquad \text{... (5)}$$

Density of states

$$g(E) = \frac{dN}{dE} = \frac{d(k^2/2\pi)}{dE} = \frac{k}{\pi}\left(\frac{dk}{dE}\right)$$

Now $\qquad E = \dfrac{\hbar^2 k^2}{2m}$ (along free directions)

$\therefore \qquad k = \sqrt{\dfrac{2m}{\hbar^2}}\; E^{1/2}$

$$\therefore \qquad dk = \sqrt{\frac{2m}{\hbar^2}}\,\frac{1}{2}\,E^{-1/2}\,dE$$

Substituting the values of k and dk in the above expression, we get

$$g(E) = \frac{1}{\pi}\left(\frac{2mE}{\hbar^2}\right)^{1/2} \times \left(\frac{2m}{\hbar^2}\right)^{1/2} \frac{1}{2}E^{-1/2}$$

or

$$g(E) = \frac{m}{\pi\hbar^2} \qquad \text{... (6)}$$

This is the energy density of the subband for a given k_z (or E_n). For each successive k_z there will be an additional $m/\pi\hbar^2$ term and hence another subband. The density of states is therefore expressed as

$$g(E) = \frac{m}{\pi\hbar^2}\sum_n \Theta\,(E - E_n) \qquad \text{... (7)}$$

where Θ is the Heaviside function or unit step function and is given by

$$\Theta\,(E - E_n) = \begin{cases} 0 & \text{for} \quad E < E_n \\ 1 & \text{for} \quad E > E_n \end{cases} \qquad \text{... (8)}$$

The plot of $g(E)$ versus E for a two-dimensional material like quantum well is shown in fig. 4.4. The resulting density of states for a quantum well is a **staircase.**

Clearly in each subband, the density of states is a constant *i.e.,* independent of energy. The difference in the density of states of two consecutive sub-bands is $m/\pi\hbar^2$.

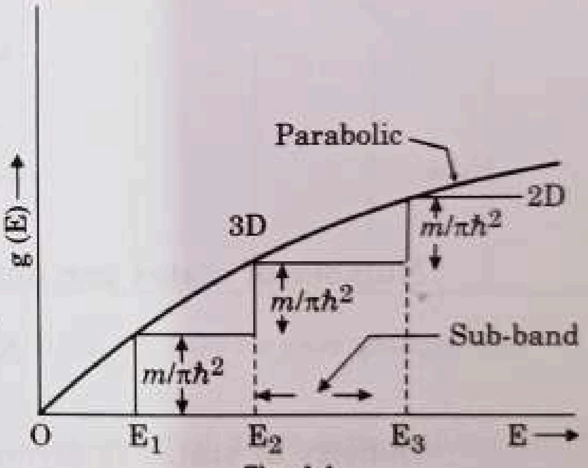


Fig. 4.4.

4.4. DENSITY OF STATES IN ONE DIMENSION (QUANTUM WIRE)

In a one dimensional material such as a quantum wire, particle motion is confined along two directions (say y, z) and free along one direction (say x). Thus there is only one degree of freedom. Particle energy is quantized for motion along y and z directions. Total energy of the system can be written as the sum of the energy along the quantized directions (y, z) and the energy along the free direction (x), *i.e.,*

$$E = \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m} + \frac{\hbar^2 k^2}{2m} = E_l + E_n + E_x \qquad \text{... (1)}$$

where $k = k_x = \dfrac{2\pi}{L_x}$. For the confined directions, we have

$$k_y = \frac{l\pi}{L_y}$$

$$k_z = \frac{n\pi}{L_z}$$

where $l, n = 1, 2, 3, \ldots$ are integers. We consider a length $2k$ in k-space. The number of modes (states) along this length

$$= \frac{2k}{k_x} = \frac{2k}{2\pi/L_x} = \frac{k}{\pi} L_x$$

If the particle be an electron then there can be two electrons one with spin up and other with spin down, corresponding to each energy. Therefore the number of states along the length k_x is

$$= 2 \times \frac{k}{\pi} L_x = \frac{2k}{\pi} L_x$$

∴ Number of states per unit length

$$N = \frac{\frac{2k}{\pi} L_x}{L_x} = \frac{2k}{\pi} \qquad \ldots (2)$$

Now $$k = \sqrt{\frac{2mE}{\hbar^2}}$$

∴ Number of states per unit length

$$N = \frac{2}{\pi} \sqrt{\frac{2mE}{\hbar^2}} \qquad \ldots (3)$$

∴ Density of states is given by

$$g(E) = \frac{dN}{dE} = \frac{2}{\pi} \sqrt{\frac{2m}{\hbar^2}} \frac{d(\sqrt{E})}{dE} = \frac{2}{\pi} \sqrt{\frac{2m}{\hbar^2}} \times \frac{\frac{1}{2} E^{-1/2}\, dE}{dE}$$

or $$g(E) = \frac{1}{\pi} \sqrt{\frac{2m}{\hbar^2}} E^{-1/2} = \frac{1}{\pi} \sqrt{\frac{2m}{\hbar^2 E}} \qquad \ldots (4)$$

This is the energy density for a given n, l value or (E_n, E_l combination). This clearly shows that **the density of states of a one dimensional system (quantum wire) decreases with increase in energy for every (n, l) combination.**

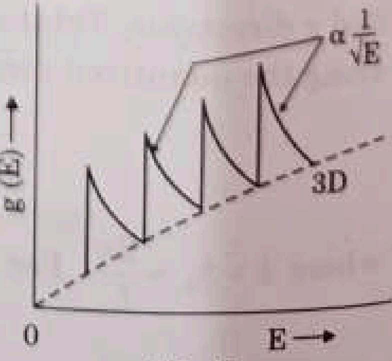


Fig. 4.5.

By taking into account all n, l combinations, the complete expression for density of states is expressed as

$$g(E) = \sqrt{\frac{2m}{\pi^2 \hbar^2}} \sum_{n,l} \frac{1}{\sqrt{E - E_{n,l}}}\, \Theta\ (E - E_{n,l}) \qquad \text{... (5)}$$

where $\Theta\ (E - E_{n,l})$ is the Heaviside or unit step function. The plot of $g(E)$ versus E for a quantum wire is shown in Fig. 4.5.

4.5. DENSITY OF STATES IN ZERO DIMENSIONAL SYSTEM (QUANTUM DOT)

In the extreme case of confinement along all the three directions, particle is not free to move at all. Its motion is confined along all the three directions x, y, z. The resultant material or nanostructure is called a quantum dot or nanoparticle. The energy of the particle is quantized along all the three directions x, y, z. Therefore total energy of the system is quantized and is given by

$$E = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m} = E_l + E_n + E_p \qquad \text{... (1)}$$

$$\delta(x) = \begin{cases} +\infty, & x = 0 \\ 0, & x \neq 0 \end{cases}$$

where $l, n, p = 1, 2, 3, \ldots$ are integers.

Also

$$k_x = \frac{l\pi}{L_x}$$

$$k_y = \frac{n\pi}{L_y}$$

$$k_z = \frac{p\pi}{L_z}$$

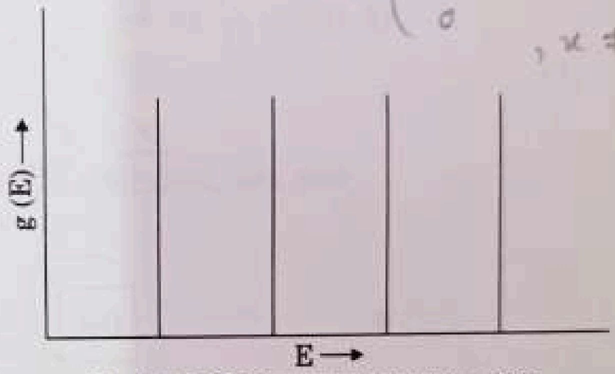


Fig. 4.6. DOS for Ideal quantum dots

In this case there is no k-space to be filled with electrons and all available states exist only at discrete energies. Hence the density of states for a zero dimensional (0D) system *i.e.*, a quantum dot is expressed by a delta function as

$$g(E) = \delta(E - E_{n,l,p}) \qquad \text{... (2)}$$

Fig. 4.6. shows the plot of $g(E)$ versus E for a zero dimensional material.

In real quantum dots, the size distribution leads to a broadening of the delta (line) function as shown in the Fig. 4.7.

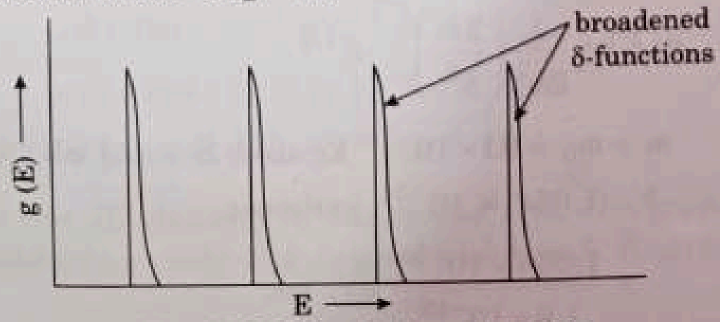


Fig. 4.7. DOS for Real quantum dots

4.6. COMPARISON OF DOS FOR 3D, 2D, 1D AND 0D NANOSTRUCTURES

The variation of density of states (DOS) with energy for bulk, quantum well, quantum wire and quantum dot is shown below :

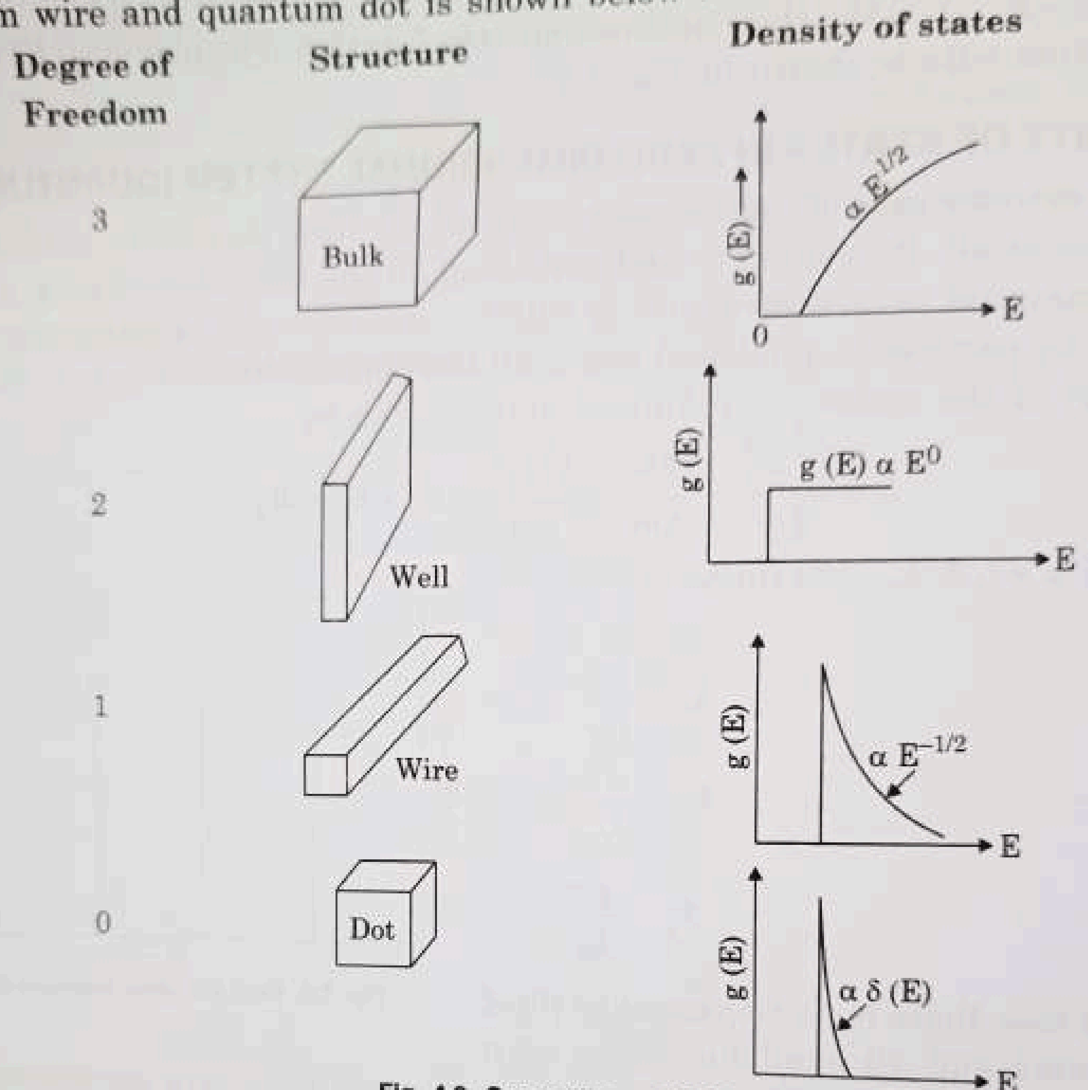


Fig. 4.8. Comparison of DOS

Solved Examples

Ex. 1. ***Calculate the density of states of electrons of energy 0.1 eV in three dimensions. Express the result in terms of eV and cm^3.***

Sol. The electronic density of states in three dimensions is given by

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \qquad \text{... (1)}$$

Given that,

$$m = m_0 = 9.1 \times 10^{-31} \text{ kg and } E = 0.1 \text{ eV}$$

$$\hbar = 1.054 \times 10^{-34} \text{ joule-sec}$$

$$= \frac{1.054 \times 10^{-34}}{1.6 \times 10^{-19}} \text{ eV. sec}$$

$$= 0.65875 \times 10^{-15} \text{ eV.sec.}$$

Environment : The nature of the nanoparticles synthesized is greatly affected by the surrounding environment. During biological synthesis, the nanoparticles form a coating that makes them thicker and larger sized. The environment also influences the physical structure and chemistry of the synthesized nanoparticles.

Besides the above discussed factors, there are certain other parameters (or factors) that greatly influence the nature of nanoparticles being synthesized.

5.3. TOP-DOWN APPROACHES

Top-down approaches of synthesizing nanomaterials use macroscopic initial structures, which can be externally controlled in the processing of nanostructures. Typical examples are etching through the mask, ball milling, cutting, grinding and application of severe plastic deformation, photolithography, *e*-beam lithography etc.

Top-down methods begin with a pattern generated on a larger scale, which is reduced to nanoscale after a sequence of operations is performed over them. The **major drawback** of these methods is that they require large installations and huge capital is required for building their set-up. Therefore these methods are **quite expensive**. Moreover the **growth process is slow** and hence these methods are not suitable for large scale production. However top-down methods are very suitable for laboratory experimentation.

Top-down approaches are based on grinding of material. Thus these processes are subtractive in nature. The parts of mechanical devices used to shape objects are stiff and hard, so these methods are **not suitable for soft samples**. The top-down approach anticipates nanodevices that must be built piece by piece in a number of stages, much like manufactured items are made. Scanning probe microscopy (SPM)

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nano-e
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cutting
place.

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is an important technique used both for synthesis and characterization of nanomaterials by top-down approach. Atomic force microscope (AFM) tips can be used as a nanoscale "write head" to deposit a resist, which is then followed by an etching process to remove material in a top-down method. **Very high quality thin films can be deposited** with nanometer control perpendicular to the plane of a substratum and this method is called **physical vapour deposition (PVD)**. In this method the material to be deposited is evaporated from the reservoir or sputtered from the target.

Chemical vapour deposition (CVD) is another technique for the synthesis of nanostructures using top-down approach. In this method, the precursor (which is a compound that participates in a chemical reaction that produces another compound) of the thin layer is a reactive gas or mixture of gases and the substratum is typically heated to accelerate chemical reaction to form a solid product deposited as a film. The decomposition can be enhanced with a plasma. In MOCVD, the growth of crystals is by chemical reactions instead of physical deposition (as in MBE).

Metal-Organic Chemical Vapour Deposition (MOCVD) also known as Vapour Phase Epitaxy (MOVPE) takes place not in a vacuum, but from the gas phase at moderate pressures (2 to 100 kPa). This is a **suitable technique for growing compound semiconductors** from the surface reaction of organic compounds and metal hydrides containing the required chemical elements.

Ion implantation is used to modify existing surfaces of materials. In this method, electrostatically charged high energy (10-100 Kev) ions are directed towards the surface, where they arrive with kinetic energies several orders of magnitude higher than the binding energy of the host material, and become implanted in a surface layer that may be tens of nanometers thick.

In the top-down approach nano-objects are obtained from larger entities without atomic level control. Many technologies that emerged out of conventional solid state silicon methods for fabricating microprocessors are now capable of creating features smaller than 100 nm, which lie in the domain of nano-technology. Giant magneto resistance (GMR) based hard drives which have been already commercialized use top-down approach. Top-down methods can also be used to create nano-electromechanical systems (NEMS). Top-down methods use lithography in which a bulk material is reduced in size to nanoscale pattern. In top-down approach cutting, milling and shaping of materials into the desired shape and order takes place.

Electron beam lithography and **X-ray lithography** have been developed as an alternative to photolithography technique used in top-down methods. However electron beam technique is very expensive and also very slow. In top-down methods the starting material is generally solid. In these methods the material suffers an **increase in surface defects** since the material is subjected to internal stress.

5.4. BOTTOM-UP APPROACHES

Bottom-up approaches of synthesis of nanomaterials include the miniaturization of materials components to atomic level with further self assembly process leading to the formation of nanostructures. During self assembly the physical forces operating at nanoscale combine basic units into larger stable structures. Typical examples are quantum dot formation during epitaxial growth and formation of nanoparticles from colloidal dispersion, physical vapour deposition, chemical vapour deposition etc.

In the bottom-up methods we start with atoms or molecules and build nano-structures by the direct manipulation of atoms or molecules. *Bottom-up methods involve atom-by atom, molecule-by-molecule or cluster-by-cluster manipulation for synthesis of nanostructures.* In these methods the starting material is either in liquid state or gaseous state. These techniques include chemical synthesis, self-assembly and positional assembly. Dual polarisation interferometry is one tool suitable for characterization of self assembled thin films.

Bottom-up approach is **based on the principle of molecular recognition** (*i.e.*, self assembly). Self assembly means growing more and more things of one's kind from themselves. The idea of self assembly (shake and bake) is to gather precursors in random positions and orientations and supply energy (shaking) to allow them to sample configuration space. The hugeness of this space suggests that a convergent pathway is inherent in the process in order to allow it to be completed in a reasonable time. Once the precursors are in position, "baking" may be required to strengthen the bonds connecting them and fix the final object permanently.

Many biological systems exhibit remarkable capabilities of assembling themselves starting from a randomly arranged mixture of components. The examples are bacteriophage virus, and proteins and ribonucleic acids (RNA) which can be spontaneously transformed from a random coil of the linear polymer to a compact, ordered 3D structure. In this approach the starting precursors of the final structures have to be very carefully designed.

The highly specialized chemistry of living systems, the fragility of many of its products and its inherent variability at many levels have made self assembly unsuitable for mimicking directly and incorporating into our present industrial system.

Bottom-up approaches are **capable of producing devices in parallel** and **much cheaper than top-down methods** but becomes difficult as the size and complexity of the desired assembly increases. Most useful structures require complex and thermodynamically unlikely arrangements of atoms. Watson-Crick base pairing and enzyme substrate interactions are notable examples of self assembly based on molecular recognition in biology. Approaches from the field of "Classical Chemical" synthesis also aim at designing molecules with well defined shape. AFM tips can be used as a nanoscale "write head" to deposit a chemical upon a surface in a desired pattern in a process called **dip pen nano-lithography.**

In the bottom-up methods high precision actuators (devices that convert electrical energy to mechanical energy and vice-versa) move atoms from place to place. Micro tips such as AFM tips emboss or imprint materials. Electron or ion beams are directed onto the surface at which device is to be grown.

Nature uses self-assembly in ultra-fine ways. The natural world is self assembled. In nature, spontaneous organization of molecules into stable, structurally well defined aggregates of nanometer dimensions takes place. Molecules can be transported to surfaces through liquids to form self-assembled monolayers (*i.e.* single atom thick layers). Atomic layer deposition (ALD) is one of the bottom-up methods which is very useful in depositing thin atomic layers on a substrate. Bottom-up methods provide improved nanostructures with less or defect free, homogeneous and long and short range orders.

5.5. BALL MILLING

A ball mill is a device used to grind and blend materials for use in mineral dressing processes, paints, pyrotechnics, ceramics and selective laser sintering. It is a **physical method of synthesis of nanoparticles** and is an example of **top down approach** of producing nanomaterials.

The ball mill consists of a hollow cylindrical shell which rotates about its axis. The axis of the shell may be either horizontal or inclined at a small angle to the horizontal. It is partially filled with the balls which may be made of chrome steel, stainless steel, ceramic or rubber. These balls form the grinding media of the ball mill. The inner surface of the cylindrical shell is generally lined (*i.e*, coated) with an abrasion resistant material *e.g.*, rubber or mangenese steel. Rubber is preferred for this purpose due to less wear in mills lined with rubber. The length and diameter of the ball mill are nearly equal.

Principle : A ball mill works on the **principle of impact and attrition** (*i.e.* friction). The size reduction is carried out by impact as the balls drop from near the top of the shell. In a continuously operated ball mill, the material to be ground is fed from the left through a 60° cone and the resulting material (product) is discharged through a 30° cone to the right both not shown in the figure 5.2. With the rotation of the shell, the balls are lifted up on the rising side of the shell and then they drop down on to

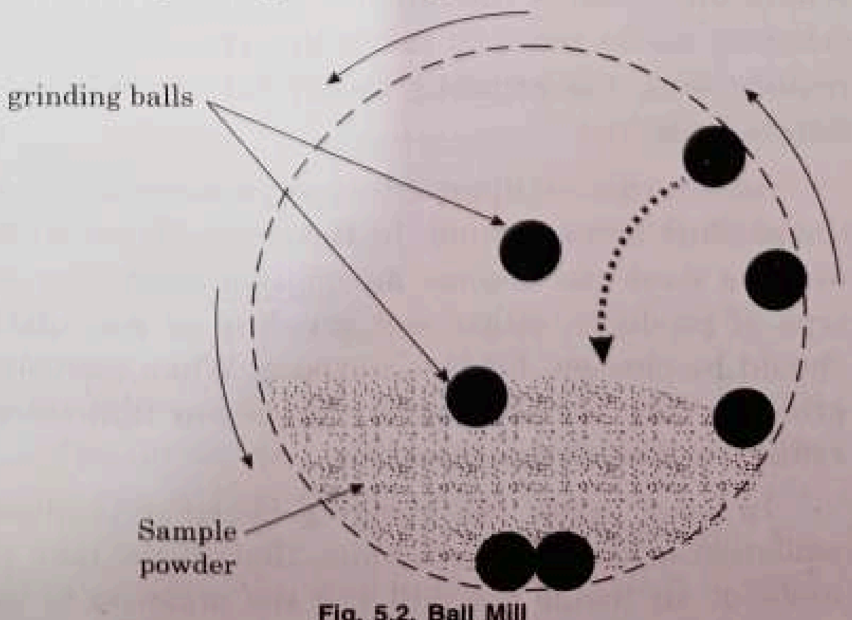

Fig. 5.2. Ball Mill