

→ Functionality \propto no. of atoms

\propto surface to vol ratio

$$\propto \frac{1}{\text{size of material}} = \frac{\text{no. of atoms on surface}}{\text{Total no. of atoms}}$$

→ So, all the solid materials are classified into 3 basics.

1. Metals }
2. Ceramics }
3. Polymer }
classification is purely based on
chemical composition &

Metals

→ Metals are classified based on their densities & the metallic elements are Ni, Co, Pt.

Non-metallic elements are C, O, N

Metals

Pt

Density (g/cm³)

21.5

Ag

10.5

Cu

8.96

Fe/Steel

7.87

Ti

4.51

Al

2.7

Mg

1.74

Ceramics :

ZnO — 5.86

Al₂O₃ — 3.6

SiC — 3.2

Glass — 2.2

Polymer

PTPE — 2.2

PVC — 1.32

Rubber — 1.34

Composites

GFRC — 1.8

Wood — 0.65

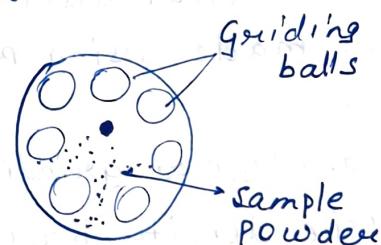
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AFM

→ classification in terms of density of state & chara. using XRD
→ solid state
→ sol gel
→ Hydrothermal

→ Ball Milling:

- ball is used to crush the materials
- grinding media → material of ball & crushed material
- most versatile method used in industries.
- it consists of hollow cylindrical shell which rotates about its axis,
this axis may be vertical or horizontal
& doesn't have to be.
- here axis of rotation of balls is aligned to axis of shell rotation.



critical speed $\rightarrow n_c$

so, ball should have speed greater than critical speed (n_c)

$$\rightarrow n_c = \frac{1}{2\pi} \sqrt{\frac{g}{R-r}}$$

R → radius of shell

r → radius of balls

→ Requirements:

- i) final size of the end product. (x) → grinding balls should be small
- ii) hardness of the material.
- iii) its flammable or non-flammable material.
- iv) cost

→ 1st principle of ball milling:

- It works on principle of impact & attrition, so the size reduction is made as near the top of the shell.
- for continuous operating mill is need to be a feed from the left in a cone shaped at 60° , right $\rightarrow 30^\circ$ cone (out)

so the grinding of the material works on the critical speed, speed after which steel balls start rotating along the direction of the cylindrical device. ω_c is speed (to grind $< N_c$)

→ Ball milling can grind materials upto size of 5 nm.

→ issue is crystallinity, only polycrystalline particle can be made using Ball milling. (Amorphous).

→ Many type of grinding media can be used based on requirements (size, density, hardness, composition)

→ smaller the media particles \Rightarrow smaller will be the size of end products.

grinding media particles should be substantially larger than the size of particles which have to be ground.
(go in steps) ($> 100 \mu\text{m}$)

→ density of the grinding media should be more than density of materials to be grinded.

→ grinding media should be hard enough to grind the material.

→ for various grinding applications when the colour of end product is imp then colour of grinding media should be taken into consideration.

→ mostly tungsten is used bcoz it is hard & inert.

→ in order to grind flammable materials, grinding media should be wet or use a inert environment. (Ar, N_2) / Steel \times bcoz it can ignite

→ in order to avoid contamination, use the media also of the same material.

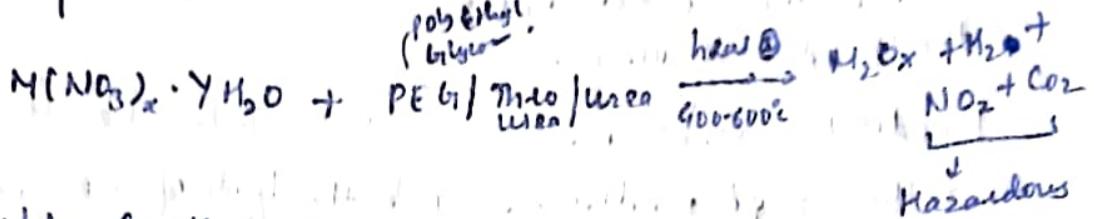
→ critical speed role in grinding media.

- Potential use of Ball milling → ^{metals} _{demeats}
- justify why tungsten balls are used?
- justify why products from Ball milling are amorphous
- without any contamination?

Date - 16/01/25

Solid state Method synthesis-

→ To form Oxide will be the final product. M_2O_x .



→ Highly Exothermic.

→ will take less time to take or perform.

→ size reduce of material (Pdt)

→ by Pdt of single crystalline nano particle.
 will be size

→ nanoparticle < 30 nm.

→ Terminology will be simple but highly conceptual.

→ Copper + Nickel

(Deposition) for prepare CNT

} water
plasmonic

In Research

"You are good for Nothing, but I will use you for H₂ production

mentally presence"

Q Advantage & Disadvantage of SSP

Q State that why SSP process is preferred?

by ball milling.

↳ for large process → ball milling.

for fine crystalline pdt → SSP.

Q Explain the role in electrolyte process.

Hydrothermal:

Phase transition diagram of pressure and temperature.

$P \uparrow T \downarrow$

Sol-gel & Hydrotherm

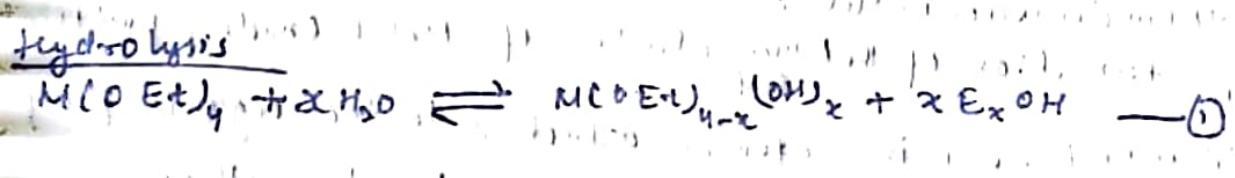
\rightarrow sol-gel \rightarrow Atmospheric pressure

\hookrightarrow for Reactant as a Nitrate.

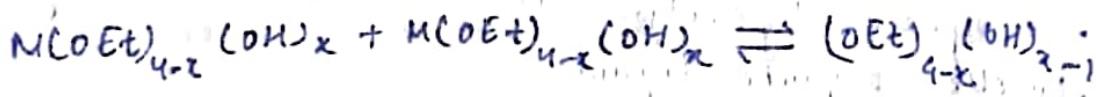
Sol-gel is best than solid-state route when you are comparing chemical uniformity.

sol-gel $>$ hydrothermal $>$ solid-state $>$ ball-milling.

Hydrolysis
 \rightarrow Condensation



Condensation



These eqn for both 'Sol-gel' as well as 'Hydrothermal'.

Sol-gel

is next chemical route for the synthesis of colloidal or inorganic-organic dispersion of organic and inorganic or hybrid material. Of purely oxide and oxide based hybrid.

- Ques: Deodorant, spray paints.
 → colloidal suspension is used for the coating.
- From such colloidal dispersion porous films, thin film, membranes can be prepared.
 - Sol-gel has many process advantage like
 - ① Low processing temperature
 - ② "Molecular homogeneity."

Condensate reaction: $M = M_1 \& M_2, Et \rightarrow Ethyl$

→ $M(\text{NOEt}) \rightarrow$ metal Ethyl component

→ In sol-gel using organic components.

we are

→ As to Rxn 1st and 2, is a multisteps process.
 either occurred sequentially or occurred parallel.

Condensation result:-
 formation of the Nano-clusters of Metal Oxide; particle
 either embedded in or attached to the organic group
 these organic group are present due to either
 incomplete hydrolysis or induced as a non-hydro-
 lyzable organic ligands!

Note: In this process size of Nano-clusters and
 morphology of the final pdt is controlled by
 the Hydrolysis and condensation reaction

→ Calcination
 → organic contamination is removed.
 → remove weight is $(Et)_2$.

- Metal reactivity is depend largely on the extent of the charge transfer and ability to increase its coordination no.
- Size is related to the C.No.
- "As a thumb rule" ^{as on} Electronegativity of a metal decrease ability to increase its coordination number. with their ionic radius.
- ionic radius ↑ Electronegativity ↓ C.No. ↑

↳ P^{MAX}
TransitTo-Metal.
thats why.

20. 01. 25

- Unfilled d-orbitals → faster e⁻ transfer

Pt →

↓ { Co
Ni
Fe
bottom gr. elements

Ni/Co/C

→ Nano sized

→ Low cohesion energy

→ Surface to vol. ratio

→ High conductivity

↓
conductivity is due to σ-bonds (in planes of 2D)
π-bonds (out of plane bonds, along z-axis)
↳ non-conducting → 2D materials along c-axis

Formation of 1D sto. :

1. Spontaneous Growth
2. Template Growth > 2 types of techniques

Spontaneous Growth:

Template Growth

- Electroplating & electrophoretic
- Colloidal dispersion, melt.
- Conversion with chemical sea
- Electrospraying

3. Electrospinning

4. Lithography

$\rightarrow \Delta G = 0 \rightarrow$ saturation

$\Delta G < 0 \rightarrow$ possible

$\Delta G > 0 \rightarrow$ "not possible"

"sea" द्वारा की ओर
इसके पास चलेगा

$$\rightarrow \frac{dP}{dT} = \frac{-L_H}{T(V_2 - V_1)}, \quad L_H = \text{latent heat}$$

Raoult's - Raoult's refn.

"> कीरण फॉर्म द्वारा"

$$\rightarrow J = \frac{\alpha \sigma P_0}{\sqrt{2 \pi m k T}} \xrightarrow{\text{pressure}} \text{tells about rate/size}$$

Maxwell's 4 eqns.

(atoms/cm²)
sec.

\rightarrow To ~~need~~ grow good crystalline materials, you need a high pressure, so hydrothermal is good.

\rightarrow Evaporation & dissolution are also k/a vapour-solid (vs) process. Driving force for this process is Gibb's free energy.

\rightarrow In case of nanowires/nano rods, the spontaneous growth G dec. by either recrystallization or by dec. in super saturation. This is called anisotropic growth i.e. growth will occur at diff. rate along diff. crystallographic directions & the crystallographic dir^s are generally {111}, {110}, {100}

(h k l) {h k l} < h k l > [h k l]

↓
planes

↓
family of planes

↓
dir

↓
family of dir

→ $\{111\}$ has always a greater growth rate than

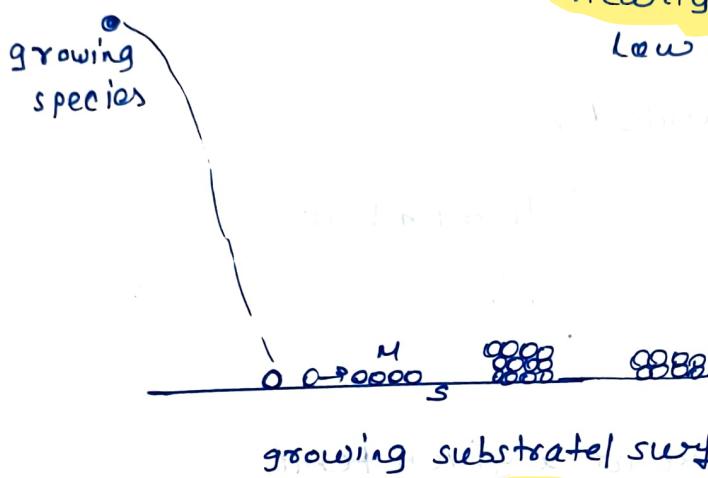
- Length of the growth is controlled by the easy direction of growth i.e. along which anisotropic energy is low.
atoms diffuse either through vacancies or interstitial gaps
- * Bulk
 - * Surface → Diffusion
 - * Sub-surface → atoms move along below one or two atomic layers

surface > subsurface > bulk
↳ vacancy > interstitials

1. Diffusion of the growth species from bulk to the growing surface/substrate
 - objective is to bring the growing species into atomic form. if $M-M$ interaction energy $>$ equal \rightarrow perfectly crystalline growth.
 - This can decide the nature of growth, but isn't a rate limiting (or deciding) step)
2. This process can be rate limiting step. of supersaturation or condensation

→ VS growth is carried in following steps:

- i) diffusion of growth species from bulk to the growing surface / substrate
(source should in form of atoms & this can be achieved chemically or thermally)
(layer, mixed, column growth → is decided by metal to substrate interaction energy & cohesive energy of the metal (M))
if this energy is high → stop
nearly equal → perfect growth
low → atoms move)



- ii) adsorption or desorption
(only at surface)
- iii) surface diffusion of adsorbed surface species
(during surface diff. process, growth species can either adsorb or may be incorporated to the growth sites which contribute to crystal growth or escape from the surface)
- iv) surface growth rate by irreversibly incorporate the adsorbed species into the crystal, & this is possible if supersaturation is present, this step determine the growth rate.

As a byproduct, chemicals are generated by on the surface during the growth & these byproduct are diffused from the growth surface.

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$$\left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$$

$$\begin{matrix} S & V \\ T & V \\ S & P \\ T & P \end{matrix}$$

$$\phi_e = \frac{\alpha_e N A (P_e - P_h)}{\sqrt{2\pi M R T}}$$

$$\approx 3.513 \times 10^{22} \frac{P_e}{\sqrt{M T}} \text{ molecules/cm}^2 \text{ sec}$$

$$760 \text{ torr} = 1 \text{ atmosphere}$$

$$\approx 10^3 \text{ mbar}$$

$$= 1 \text{ bar}$$

$$P_e = 1 \text{ m torr}$$

P_e → equilibrium pressure at a given temp.

P_h → hydrostatic pressure acting on the evaporate

P_t → atomic pressure/base pressure

Considering, $\alpha_e = 1$

→ If vapour pressure is more \Rightarrow no. of vapours are more
+ If this pressure is less \Rightarrow stream is generated.

$$T_e = 5.834 \times 10^{-2} \sqrt{\frac{M}{T}} P_e$$

$P_e, T_e, N_e \}$ eq. Pressure, temp & volume

$P \propto T \quad \}$ non-eq. pressure, temp & volume

as from Clacius- Clapyron eqn, we have

$$\frac{dP}{dT} = - \frac{L}{T(V_2 - V_1)}$$

$$\frac{dP}{dT} = \frac{\Delta H(T)}{T \Delta V}$$

$\Delta V = V_V - V_c$
 vapour \downarrow Condensed pressure from
 pressure where vapour was originated

The assumption is vapour pressure is always considerable or significantly higher than the condensed vapour pressure. so we generally consider $\Delta V \approx V_V$.

$$V_V \approx \frac{RT}{P} \text{ (assumption)}$$

$H \rightarrow$ Latent heat [also depends on temp]
 or
 Heat of vaporisation

molar heat of evaporation, $\Delta H \approx H_e$

$$\Rightarrow \log P = -\frac{\Delta H_e}{RT} + I \quad \downarrow \text{integration constt}$$

if at Boiling point: P is atmospheric pressure and this point is called liquid-vapour transition.

$$\log P_{atm}(T_{boil}) = \frac{15.983}{T} + 12.409 - 0.989 \log T - 3.52 \times 10^{-6} T$$

$$\text{Arrhenius eqn } (\log A = \frac{L}{B})$$

$$N_e = \underbrace{\left(\frac{2\pi m e k T}{h^2} \right)^{3/2}}_{Nc} \exp \left(-\frac{(E-E_F)}{kT} \right)$$

$$\text{as, } G_i = H - TS \quad \text{--- (1)}$$

$$\Delta G_i = G_{i_f} - G_{i_i} \quad \text{--- (2)}$$

$$\Delta G = \Delta H - T\Delta S - S\Delta T \quad \text{--- (3)}$$

$$aA + bB \geq cC \quad \text{--- (4)}$$

a, b, c are reactant & final product

$$\Delta G = cG_C - aG_A - bG_B \quad \text{--- (5)}$$

$a, b, c \rightarrow$ stoichiometric co-efficients.

$$G_i^\circ = G_i^\circ + RT \ln a_i^\circ \quad \text{--- (6)}$$

$G_i^\circ \rightarrow$ free energy at equilibrium

$a_i^\circ \rightarrow$ effective thermodynamic concentration & this reflects the changes in free energy in a standard state.

$$\Delta G = \Delta G^\circ + RT \log \left(\frac{a_C^c (\text{equl.})}{a_A^a (\text{eq}) \cdot a_B^b (\text{eq})} \right)$$

at eq., $\Delta G = 0 \Rightarrow$ rxn stopped

$$\Rightarrow -\Delta G^\circ = RT \log \left(\frac{a_C^c (\text{eq})}{a_A^a (\text{eq}) \cdot a_B^b (\text{eq})} \right)$$

$$= RT \log K$$

eq. constn. of rxn

$$\text{or, } \Delta G = RT \ln \left[\left(\frac{a_C}{a_C (\text{eq})} \right)^c \left(\frac{a_A}{a_A (\text{eq})} \right)^a \left(\frac{a_B}{a_B (\text{eq})} \right)^b \right] \quad \text{(first order eqn)}$$

$\frac{a_i^\circ}{a_i (\text{eq})} \rightarrow$ represents if $\gamma_1 \rightarrow$ supersaturation
 $\gamma_1 < 1 \rightarrow$ subsaturation

In supersaturation, ΔG

$\frac{a_C}{a_C (\text{eq})}$ } product

$\frac{a_A}{a_A (\text{eq})}$ } reactants

$\frac{a_B}{a_B (\text{eq})}$

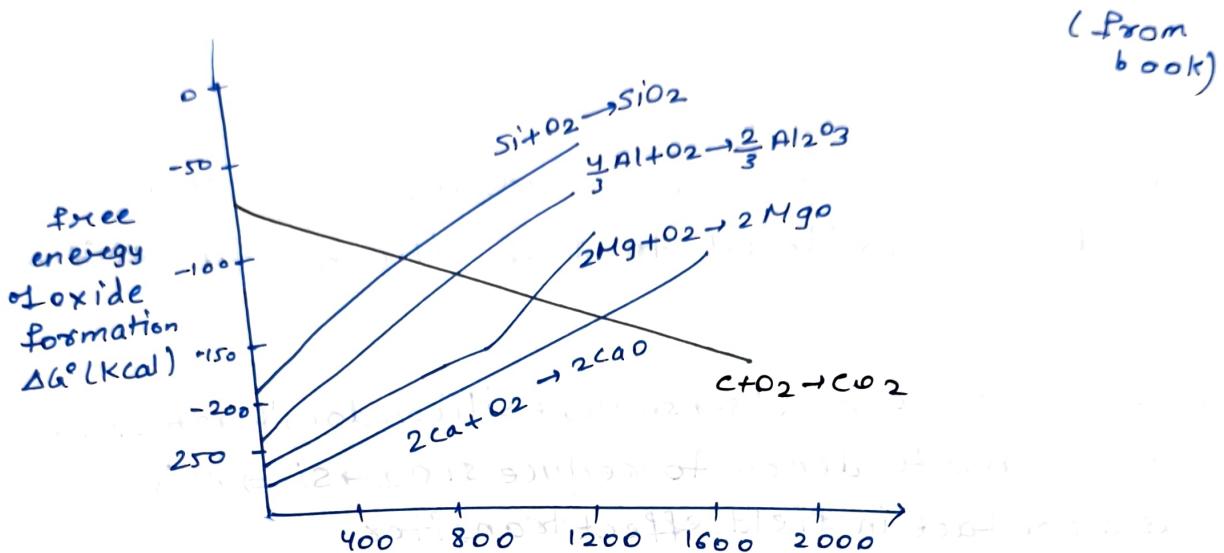


Case 1:

If there is supersaturation of reactants & subsaturation of product $\Rightarrow \Delta G < 0$ & the rxn will proceed spontaneously
 & rxn rate will depend on magnitude of ΔG .

If $\Delta G = \Delta G^\circ \Rightarrow$ then rxn will stop

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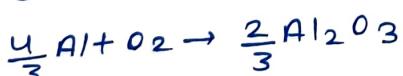
Ellingham Diagram (G-T curve)

In industries like semiconductors & industries there are two famous for semiconductors & industries

rxns

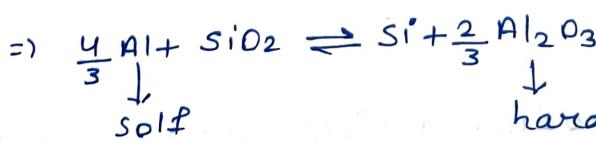


$$\Delta G^\circ_{\text{SiO}_2}$$



$$\Delta G^\circ_{\text{Al}_2\text{O}_3}$$

using elimination,



this rxn is possible according to Ellingham diagram

(bcz Gibbs free energy is -ve)

$$\Delta G^\circ = \Delta G^\circ_{\text{Al}_2\text{O}_3} - \Delta G^\circ_{\text{SiO}_2}$$

↓

(forward rxn)

$\Delta G^\circ < 0$ possible
 backward \rightarrow not possible
 $(\Delta G^\circ > 0)$

Ques] Explain the ~~complex~~ reduction of SiO_2 to Si° is possible or not in view of Ellingham diagram.

⇒ Gibbs free energy of Al_2O_3 is more -ve than that of SiO_2 ⇒ rxn is thermally favourable

at 400°C

$$\Delta G^\circ = -233 - (-180) \\ = -53 \text{ kcal/mole}$$

and bcoz of this, aluminium films are preferred to be reduced & oxidised to free silicon as a residue.

→ coating of Al → on solar cells → so that silicon doesn't get oxidised.
Al films has a tendency to reduce $\text{SiO}_2 \rightarrow \text{Si}$ ⇒ Al is used as a contact in field effect transistors

For selecting electrode → we need a material who prevent oxidation of Si & have a compatible work function.

$$K = \frac{[\alpha_{\text{Al}_2\text{O}_3}]^{2/3}}{[\alpha_{\text{Al}}]^{4/3} P_{\text{O}_2}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$

↓
pressure of oxygen (bcoz oxygen is in large amount)
& conc of oxygen is taken as unity

$$\Delta G^\circ = RT \ln P_{\text{O}_2}$$

→ if Al is vapourised to produce a field then value of P_{O_2} in equilibrium w/ both Al & Al_2O_3 can be calculated by $\Delta G^\circ = RT \ln P_{\text{O}_2}$, if actual partial pressure of oxygen exceed from eq. pressure P_{O_2} then Al will be oxidised, reverse is also true.

(and same goes for iron).

→ at 1000°C.

$$\Delta H^\circ = -202 \text{ kJ/mol} \quad P_{O_2} = 2 \times 10^{-35} \text{ atm.}$$

(value of oxygen partial pressure
in vacuum)

it means Al should be oxidised but
it doesn't happen bcz partial pressure
is 2×10^{-35} atm but in vacuum
we have high vacuum pressure
⇒ rate const of rxn becomes low.

$$J = \frac{\sigma \propto P_0 T}{\sqrt{2\pi mkT}}$$

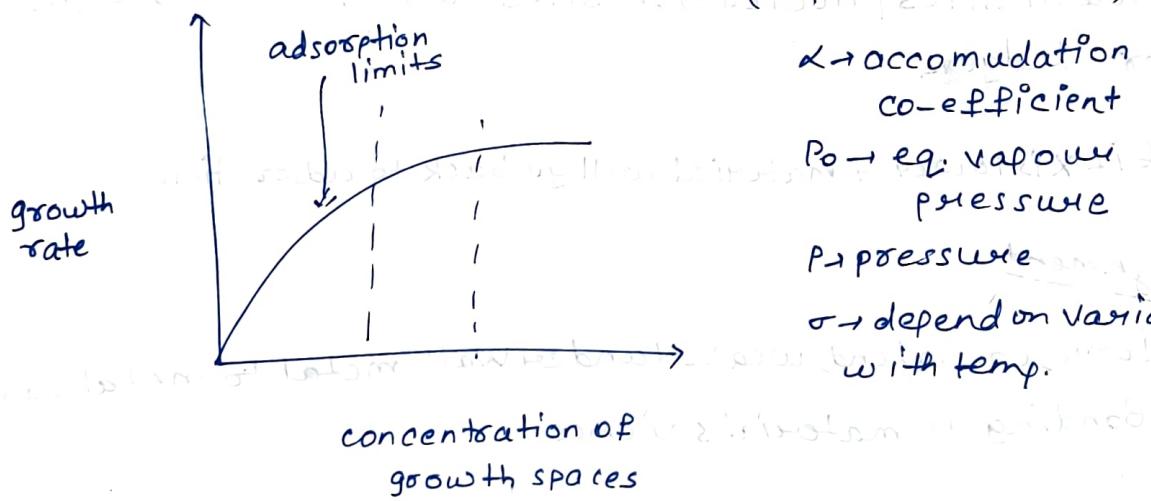
$$\sigma = \frac{P - P_0}{P_0}$$

(supersaturation)

→ accommodation
co-efficient

P_0 → eq. vapour
pressure

P → pressure
 σ → depends on variation
with temp.



→ Growth with higher α has more impact in comparison
to concentration.

→ to control α :

$$\tau_s = \frac{1}{\sigma} \exp\left(\frac{E_{des}}{kT}\right) \quad (1)$$

residence time
for growth species
on the surface

vibrational
freq of ad
atoms

E_{des} → desorption
energy required
for species to
go back
growth

(E_{des} , σ → material
properties)

i.e. adsorbed
species
on surfaces, $\approx 10^{12}$ per second

$$D_s = \frac{1}{2} a_0 \sigma \exp\left(-\frac{E_s}{kT}\right)$$

—②

diffusion rate co-efficient

$E_s \rightarrow$ activation energy for surface diffusion

$a_0 \rightarrow$ size of growth species

$$x = \sqrt{2} D_s T_s = a_0 \exp\left(\frac{E_{des} - E_s}{kT}\right)$$

$x \rightarrow$ mean diffusion distance for the growth species

NOTE:

In a crystal, x is much longer than the distance b/w growth sites/nucleation sites which is kinks edges or ledges.

(If x is lower \rightarrow material will go back to adsorption)

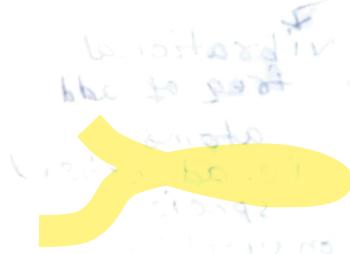
Assignment

(ionic, co-valent, weak-Vanderwall, metal to metal bonds)

Bonding in material science

no bonding in ionic form and a rapid diffusion
in covalent form, covalent bonding of
any atom has ≥ 2 bonds of

$$D_s = \frac{(2\pi b)^2 f g \sigma}{\tau} \frac{1}{C} = 25$$



adsorbents (strong adsorbents)

XRD

$$\text{as } 2ds \sin\theta = d \\ 2a \sin\theta = d \Rightarrow \frac{4 \sin^2 \theta}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2}$$

$f(hkl)$

θ	$\sin\theta$	d	$\frac{4 \sin^2 \theta}{d^2}$	$\frac{a^2}{f^2(hkl)}$
----------	--------------	-----	-------------------------------	------------------------

then search for a multiplex factor which gives a integer as a result.
A that integer will give possible value of hkl .

Assignment

→ explain for 7 crystal system, bravais lattice & corresponding formula for d-spacing.
(B.D Quality)

X-ray scattering factors:

$$F(\theta) = \sum_i f_i(\theta) \exp^{i(2\pi(h_i x_i + k_i y_i + l_i z_i))}$$

} represents intensity ratio

$(x_i, y_i, z_i) \rightarrow$ unit vector

for $F(\theta) = 0 \rightarrow$ forbidden transition.

→ indexing of peak angle

d spacing → low intensity peak.
crystallinity → high intensity peak angle

Boravis lattice	Forbidden reflection	allowed	F	No. of lattice point per unit cell	example
primitive cubic	none	any hkl	\neq	1	
fcc	hkl are mixed & even	' hkl all are odd or even	$4\neq$	4	
BCC	$(h+k+l)$ is odd	$(h+k+l)$ is even	$2\neq$	2	
fcc diamond structure	hkl are mixed & even, all even $h+k+l \neq 4n$	all even l $h+k+l = 4n$			

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CVD

depending on source of energy

- Thermal-CVD → normal heat
- Hot Wire-CVD (filament)
- MPCVD → if microwave is used
- PE-CVD → (Plasma enhanced CVD)
- MOCVD

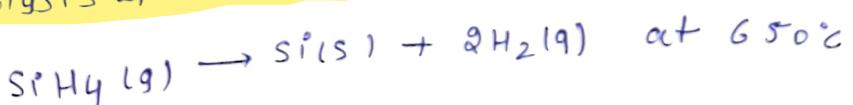
→ what type of rxns occur in CVD?

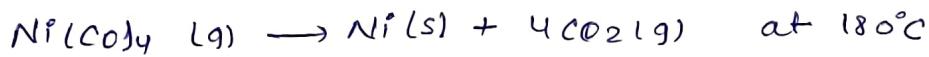
i) Pyrolysis:

→ thermal decomposition of gaseous species such as hydrides, carbonyles & organometallic compounds on the hot substrate.

ii) thermal decomposition of the solid and subsequent effluent gases, decomposition on hot substrate is called pyrolysis.

ex:- pyrolysis of charcoal → to form activated carbon.





Baggases (solid) \rightarrow activated carbon \rightarrow Effulent gas (s)

\rightarrow final product of pyrolysis rxn is solid.

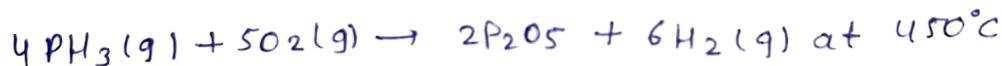
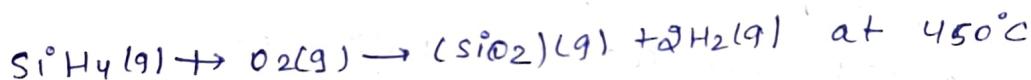
ii) Reduction:

\rightarrow best used in silicon industries.

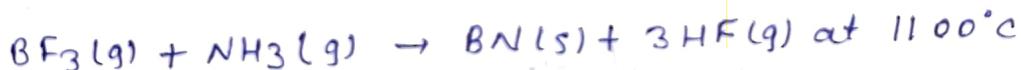


\rightarrow these two rxns are called **refractory** \rightarrow to convert minerals into a pure form.

iii) Oxidation:



iv) Compound formation: (use two type of materials & get a compound)



SiC \rightarrow large bandgap material.

BN \rightarrow second big hardest material after diamond

common rxn:



A, B, C, D → chemical species

a, b, c, d → stoichiometric ratios.

→ first check this rxn is feasible or not.

$$\Delta G^\circ = \sum_{\text{product}} G^\circ - \sum_{\text{source}} G^\circ$$

i) $\Delta G < 0$

ii) $\Delta G = 0$

iii) $\Delta G > 0$

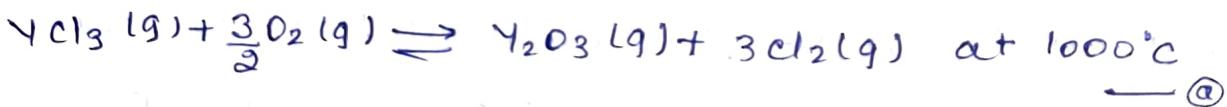
→ if $\Delta G < 0 \Rightarrow$ small negative value of G is required for the slower nucleation rate of the rxn ~~cross~~ large critical sized nuclei.

When this will occur → large amount of product & reactants simultaneously occur.

If ΔG in -ve sign is high, then large nucleation occurs
→ will leads to heterogeneous structure.

$$\left. \begin{array}{l} |\Delta G| \approx 0 \rightarrow \text{perfect crystalline} \\ |\Delta G| > 0 \rightarrow \text{polycrystalline} \end{array} \right\}$$

example:



$$\Delta G^\circ = -59.4 \text{ Kcal/moles}$$

$$\Rightarrow \log K = +13$$

This rxn is too far

$$\text{as, } -\Delta G^\circ = RT \ln K \quad \text{--- } ③$$

$$\Rightarrow \Delta G^\circ = RT \log \left\{ \frac{\left[\frac{a_c}{a_c(\text{eq})} \right]^c}{\left(\frac{a_a}{a_a(\text{eq})} \right)^a \left(\frac{a_b}{a_b(\text{eq})} \right)^b} \right\}$$



for common rxn,

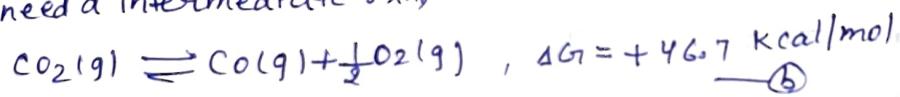
$$K = \frac{\left(\frac{a_c}{a_{c(eq)}}\right)^c \left(\frac{a_d}{a_{d(eq)}}\right)^d}{\left(\frac{a_a}{a_{a(eq)}}\right)^a \left(\frac{a_b}{a_{b(eq)}}\right)^b}$$

(for K to be high \rightarrow Unhomogenous \rightarrow not feasible for single crystal growth)

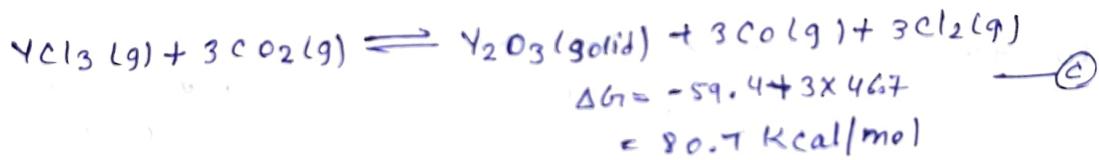
bcz of high k, this rxn is too fast for the practical film growth.

If chloride is changed to Br_x, I less stable \rightarrow they have low gibbs free energy $\Rightarrow \Delta G^\circ \text{ more -ve.}$

\Rightarrow we need a intermediate rxn,

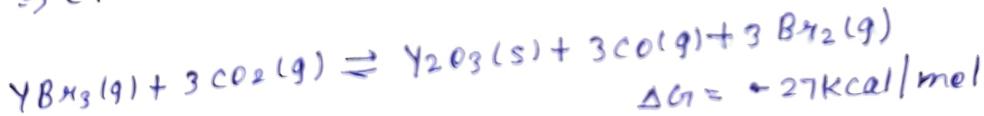


adding rxn @ & \textcircled{B} ,



\Rightarrow supersaturation case

\Rightarrow Cl has to be changed with Br_x .



Feasible rxn

\rightarrow Ques Justify the procedure for growth of Y_2O_3 , in terms of gibbs free energy identify suitable reactants

\rightarrow Si-Cl-H

$\text{SiCl}_4, \text{SiCl}_3\text{H}, \text{SiCl}_2\text{H}_2, \text{SiClH}_3, \text{SiH}_4, \text{SiCl}_2\text{HCl, H}_2$
intermediate species



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miton book}

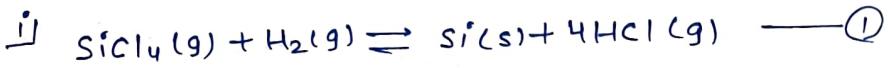
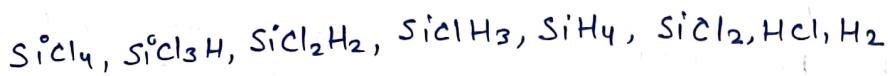
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→ CVD

→ concⁿ of reactants

→ growth reactor pressure

→ temperature



(silane gas)

(explosive & flammable \Rightarrow handling needs a good setup)

For rxn ①, rate constant becomes,

$$K_1 = \frac{[\alpha_{\text{Si}}] [\text{P}_{\text{HCl}}]^4}{[\text{P}_{\text{SiCl}_4}] [\text{P}_{\text{H}_2}]}$$

P stands for partial pressure
pressure of expected gas

similarly

$$K_2 = \frac{[\alpha_{\text{Si}}] [\text{P}_{\text{HCl}}]^3}{[\text{P}_{\text{SiCl}_3\text{H}}] [\text{P}_{\text{H}_2}]}$$

$$K_3 = \frac{[\alpha_{\text{Si}}] [\text{P}_{\text{HCl}}]^2}{[\text{P}_{\text{SiCl}_2\text{H}_2}] [\text{P}_{\text{H}_2}]}$$

$$K_4 = \frac{[\alpha_{\text{Si}}] [\text{P}_{\text{HCl}}] [\text{P}_{\text{H}_2}]}{[\text{P}_{\text{SiClH}_3}]}$$

$$K_5 = \frac{[\alpha_{\text{Si}}] [\text{P}_{\text{HCl}}]^2}{[\text{P}_{\text{SiCl}_2}] [\text{P}_{\text{H}_2}]}$$

$$\text{and } K_6 = \frac{[\alpha_{\text{Si}}] [\text{P}_{\text{H}_2}]^2}{[\text{P}_{\text{SiH}_4}]}$$

$$\begin{aligned} \text{total partial pressure} &= \text{growth pressure/reactor pressure} \\ &= 1 \text{ atm} = 760 \text{ torr} \\ \Rightarrow P_{\text{SiCl}_4} + P_{\text{SiCl}_3\text{H}} + P_{\text{SiCl}_2\text{H}_2} + P_{\text{SiClH}_3} + P_{\text{SiH}_4} + P_{\text{SiCl}_2} + P_{\text{HCl}} + P_{\text{H}_2} \\ &= 1 \text{ atm} \end{aligned}$$

considering,

$$[\text{Si}] = 1$$

now we have to calculate mole concentration of HCl + H₂.

$$\frac{c}{M} \text{ in molar ratio}$$

mole of Cl in SiCl₄

$$m_{\text{Cl}} = 4(m_{\text{SiCl}_4})$$

$$= \frac{4 M_{\text{Cl}}}{M_{\text{SiCl}_4}} m_{\text{SiCl}_4}, \text{ where } M \text{ & } m \text{ are mass & molecular weight resp.}$$

$$\text{as, } PV = nRT$$

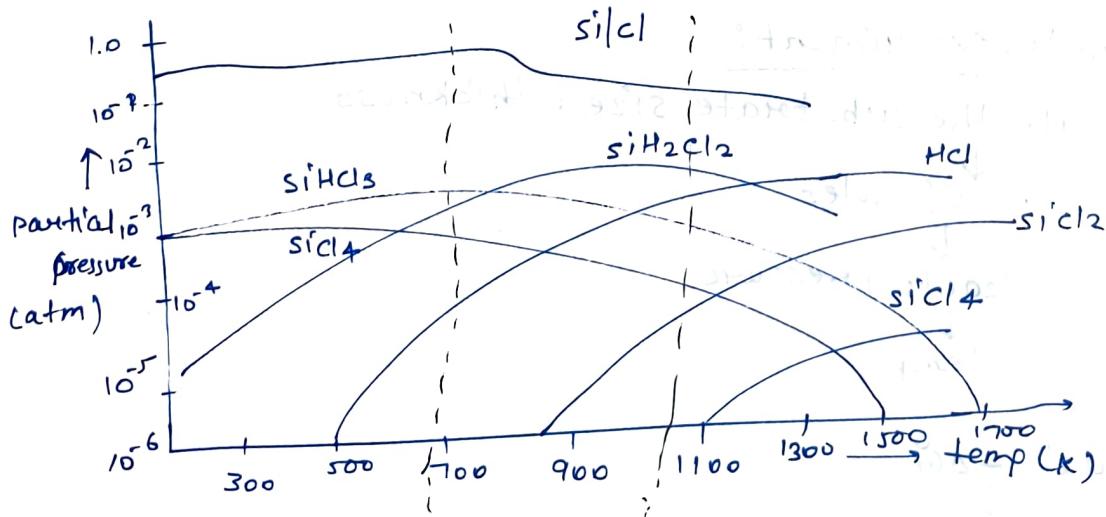
$$\Rightarrow \frac{m_{\text{SiCl}_4}}{M_{\text{SiCl}_4}} = \frac{P_{\text{SiCl}_4} \times V}{RT} \xrightarrow{\text{constt}} \text{reactor pressure}$$

$$\Rightarrow \frac{m_{\text{Cl}}}{M_{\text{Cl}}} = 4 \frac{P_{\text{SiCl}_4} V}{RT} = \text{moles of Cl} \quad \text{--- (1)}$$

as we have,

$$-\Delta G^\circ = RT \ln K^\circ \quad \text{--- (2)}$$

in CVD, at temp T $\rightarrow K^\circ$ is fixed



$$\text{for 1 atm pressure, } \frac{c}{M} = 0.01$$

Epitaxial growth, Si fixed $\Rightarrow \frac{[Si]}{[Cl]} \xrightarrow{\text{to be}} \text{fixed}$
 $\approx [Cl]$ is fixed
 $\Rightarrow \frac{[Cl]}{[H]} \text{ ratio is fixed.}$

for good quality of films, slower nucleation is preferred
 \Rightarrow (lower nucleation sites) \Rightarrow good crystallinity

for Si growth \rightarrow optimized temp is 140 K, at this Si concn is minimised & $\frac{[Cl]}{[H]}$ ratio changes to 0.01, if this ratio

changes to 0.1 then polycrystalline growth of Si occurs.

$\Rightarrow \frac{[Cl]}{[H]} = 0.01 \rightarrow$ single crystal

$\frac{[Cl]}{[H]} = 0.1 \rightarrow$ polycrystalline

$$\text{moles of } [H] = \frac{2(P_{H_2})V}{RT}$$

$$\Rightarrow \frac{[Cl]}{[H]} = \frac{2(P_{SiCl_4})}{[P_{H_2}]}$$

Concn of hydrogen can be controlled by filtrate.

→ Design the experiment:

i) calculate the substrate size & thickness

↓
no. of moles

↓
Reactor pressure

↓
temp



ii) calculate $-\Delta G^\circ$

↓
fixed $- \Delta G^\circ$

↓
calculate K

↓
calculate conc'n of reactants

(read about
space groups)

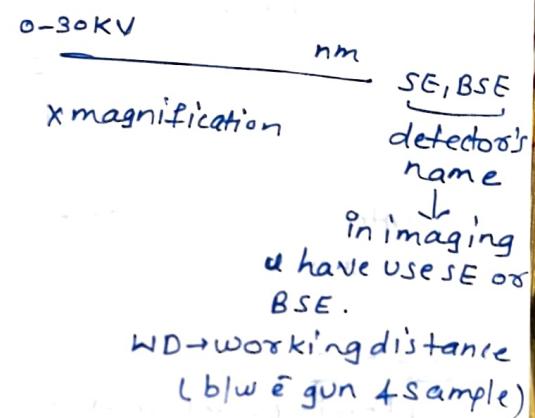
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Sputtering 4 → Renam

SEM:

if sample: metal
insulator
Polymer
biomolecule

environment → vacuum



BSE conc'n is greater than SE



(Polymer)



(used when operator saturates
due to high conc'n of BSE)

biomolecule → carbon conducting tape is used to avoid
contamination.

TEM → sample size < 100 μm [so that beam can transmit]
↓
(crystallite size)

XRD → (grain size) → if it matches with crystallite size →
perfect crystallite
< → polycrystallite.

3/2/25

structure factor: → tells which plane is allowed & forbidden

$|F_{hkl}| = \frac{\text{amplitude of wave scattered}}{\text{amplitude of } e \text{ placed at origin.}}$

$$F_{hkl} = \sum_{i=1}^N f_i e^{2\pi i (h u_i + k v_i + l w_i)}$$

→ simple cubic → $u, v, w \rightarrow 0, 0, 0$

⇒ For any hkl

$$F_{hkl} = f e^{2\pi i (h \cdot 0 + k \cdot 0 + l \cdot 0)} = f$$

$I \propto F^2 = f^2 \rightarrow$ all planes have same intensity.

→ all planes are allowed.

If intensity varies → preferred orientation.
(due to domains)

→ for BCC

atomic coordinates → $(0, 0, 0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

$$F_{hkl} = f e^{2\pi i (0)} + f e^{2\pi i (\frac{h}{2} + \frac{k}{2} + \frac{l}{2})}$$
$$= f (1 + e^{\pi i (h+k+l)})$$

for $h+k+l$
even → $F \neq 0 \rightarrow$ allowed reflections $\rightarrow F^2 \neq 0$
odd → $F = 0 \Rightarrow$ not-allowed / forbidden reflections
 $\Rightarrow F^2 = 0$

(XRD → X-ray → plane → scatter → other planes)

signature of XRD match → single crystal → intensity match
doesn't match → polycrystalline.

→ FCC

$$F_{hkl} = f (e^{\pi i (h+k)} + e^{\pi i (k+l)} + e^{\pi i (h+l)})$$

$$F_{hkl} = 4f$$

$$\text{DM} = 0$$

HCP

→ HCP Crystals (like Ru, Zn, Ti, Mg) → lattice point co-ordinates

$$(0,0,0) \quad \left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2} \right)$$

$$= F = f_i \left(1 + e^{2\pi i \left(\frac{h}{3} + \frac{2k}{3} + \frac{l}{2} \right)} \right)$$

$$\text{putting } g = \frac{h+2k+l}{3}$$

$$\Rightarrow F = f_i (1 + e^{2\pi i g})$$

$$F_{hkl}^2 = 4f_i^2 \cos^2 \pi \left(\frac{h+2k+l}{3} \right)$$

zero ⇒ $\begin{cases} h+2k \rightarrow \text{multiple of 3} \\ l \rightarrow \text{odd} \end{cases}$ ⇒ (0 0 2) plane is allowed in HCP
forbidden

→ what about solid soln alloys?

$$f_{\text{alloy}} = n_A f_A + n_B f_B$$

$n_A, n_B \rightarrow$ atomic fraction of alloy

BD Cularity

Kinematical theory

→ Materials classification. ⇒ Bar chart

→ TEM

→ dark & bright field images

→ absorption ↑ with thickness according to Beer's Law

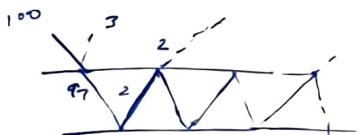
Lambert's Law

→ difference in SEM, TEM

→ Reciprocal lattice

6/2/25

- characterization of thin films
→ table 6.2 → summary of selected film techniques measurement
→ FET



→ For sustained interference, amplitude should be nearly equal.

→ Newton's ring exp → interference pattern for reflected rays.

$$2s + \frac{2\delta\lambda}{2\pi} = n\lambda$$

$$\rightarrow \text{distance b/w films} + s = \left(\frac{n-1}{2}\right)\lambda$$

$$\text{film thickness, } d = \frac{\lambda}{\text{fringe spacing}} \times \frac{1}{n}$$

successive distance b/w films

→ FECO

→ interferometry of thin films

→ $\frac{\lambda}{r} \rightarrow$ anti-coating → cond' for reflection → for solar cells etc.
(to be less)

→ VAMFO

→ 11/2/25

→ Division of amplitude → ray diagram & exp.

Fig 6.1

→ Sustained interference can be achieved by measuring in reflected modes, not in transmitted modes.

→ Ellipsometry technique

$$\Rightarrow \gamma' / n^2 = \tan \theta \quad \left. \begin{array}{l} \text{circularly} \\ \text{polarized light is used} \end{array} \right\}$$

→ Stylus Method profilometry

→ SEM → how to view information in SEM image.

→ structural charac. → fig 5.3 electron & photon signals from tear shaped interaction volume during electron-beam impingement on specimen (both a & b)

→ secondary electrons

→ backscattered electrons

→ EBSEDD

(\bar{e} beam sec. \bar{e} diffraction detector)

→ chapter: chemical characterization

table: summary of major chemical char. tech.

216 pgc Miton

Method	Electrical sensitivity	Detection limit	Lateral resoln	Effective probe depth
SEM/EDX	Na-U	~0.1	~1 μm	1 μm
AES	Li-U	~0.1-1	500 Å	15 Å
XPS	Li-U	~0.1-1	~100 μm	15 Å
RBS	He-U	~1	1 nm	~200 Å
SIMS	H-U	~10 ⁻⁴	~1 μm	15 Å

→ electron spectroscopy

Fig 6.14 → schematic of \bar{e} energy transitions

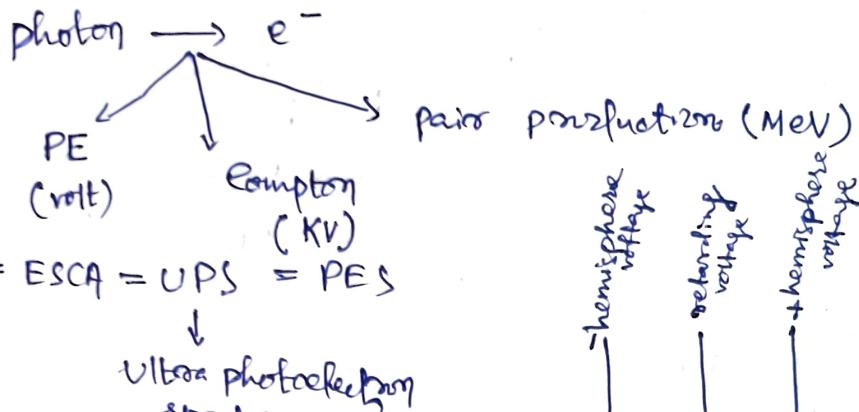
In an Auger process the following steps follows:

- i) \bar{e} are ejected from the initial level and (K-stage)
- ii) \bar{e} transition from outer level L₁ to occupy the position of hole in K-level, this resulting energy can be convert into photon but if photons are not emitted, then this energy will eject \bar{e} from the third level or above.



13.02.14

XPS



$$\rightarrow XPS = ESCA = UPS = PES$$

- # Work fun & electron affinity = energy required to eject e^- from Fermi level & form bottom of the conduction band.

$$\rightarrow \text{Pressure} \propto \frac{1}{\text{mean free path}}$$

mean free path of e^- should be high

$$\rightarrow \text{peak dose} \rightarrow \text{concentration} (\gamma)$$

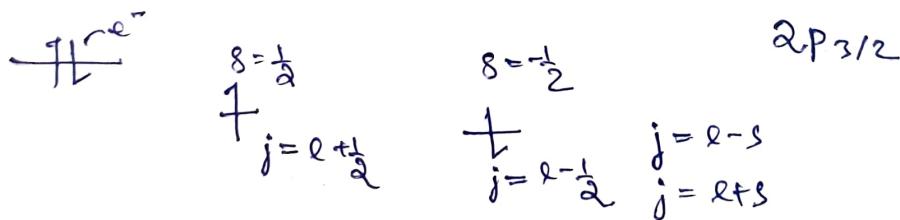
vacuum system

- Ion pump
- Turbo pump

Spin-orbital splitting

Peak notations

L-S coupling ($j = l \pm s$)



→ Diff in BE peak → which element

↳ Area ratio must be same → which state $d_{5/2}$ or $d_{3/2}$
↳ If one peak coming b/w d satellite peaks

→ Depth Profiling

$$I_s = I_0 e^{-d/l}$$

l_i = inelastic mean free path of an e^- in solid
with a path length of one λ 63% of all electrons are scattered

- Sampling depth is defined as the depth from which 95%.
- Depth profiling \rightarrow 100A° take hole hai & for multi layered str., diff b/w each layer is $\sim 3\text{A}^\circ$. So, 30 layers take ki info mtlgi, usse se jyada nahi.
- detector at ~~particular~~ किसी energy से वह accurately step size ~~concerned~~ measure कर पाएगा. So, narrow peaks identify किसी तरफ जो उनकी गति नहीं है।
- Shift in XPS