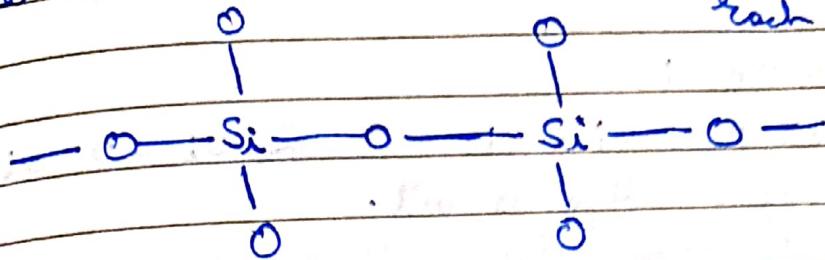


* Structure:

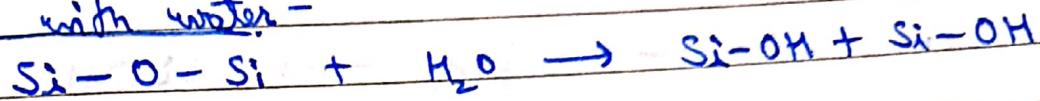
Tetrahedral structure.



Each Si to 4 O

Each O to 2 Si

→ Reacting with water -



Si-OH termination is stable.

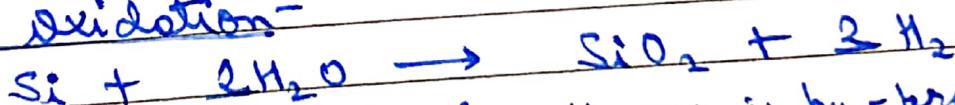
Structure is more porous than Si-O-Si.

i) Dry Oxidation -



- Dense oxide formed. (good quality, non-porous)
- Slow growth rate.
- Need to keep water out of system.

ii) Wet Oxidation -



- Porous oxide formed (as H_2 gas is by-product)
- Faster growth rate (as H_2O affects larger area)
- (Also due to intermediate stage formation)

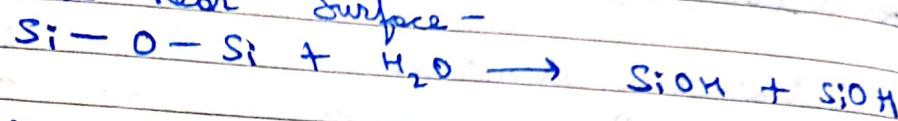
→ Although wet oxidation is faster, yet dry oxidation is preferred, as it is non-porous, hence doesn't form any area for trapping charges.

Sr. No.

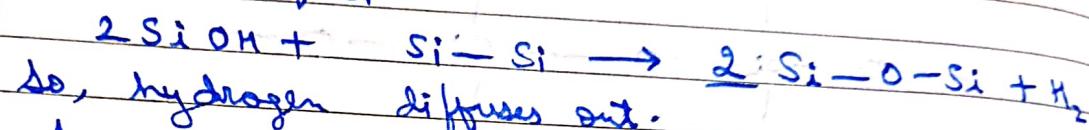
Sr. No.

* Mechanism for Wet Oxidation-

1. Hydration near Surface -

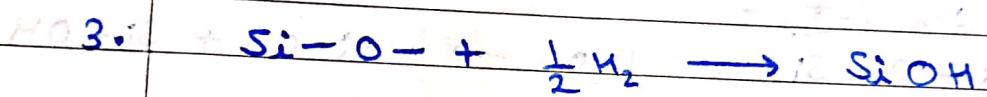


2. Oxidation of Si -



so, hydrogen diffuses out.

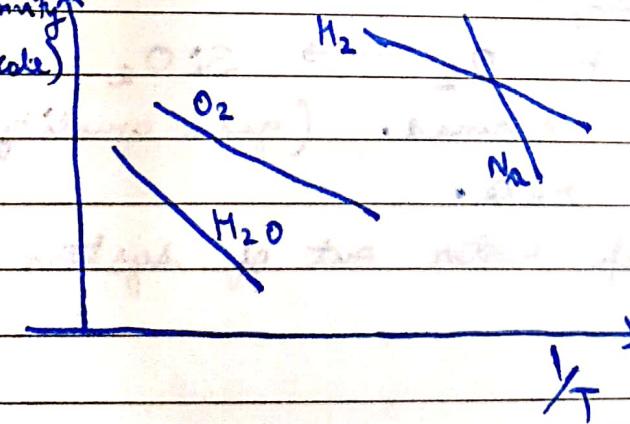
Some H_2 may form hydroxyl group.



⇒ Diffusivities in Dioxide -

Oxygen diffuses faster than Water.

Diffusivity
(log scale)



Na & H_2 diffuse very fast.

Kinetics of Oxidation

* Diffusion (J) = $-D \frac{dN}{dx}$
 $\approx \frac{D(N_o - N_i)}{x}$

Reaction rate = $k N_i$

At steady rate, $N_i = \frac{D N_o}{k x + D}$

Flux at steady rate $\rightarrow J = \frac{D N_o}{x + D/k}$

Side growth rate = $\frac{dx}{dt}$

Flux / # oxidizing species per unit Vol. of SiO_2 (J/n)

$$n_{\text{O}_2} = 2.2 \times 10^{22} \text{ cm}^{-3} \text{ for O}_2$$
$$= 4.4 \times 10^{22} \text{ cm}^{-3} \text{ for H}_2\text{O}$$

$$\frac{dx}{dt} = \frac{D N_o}{x + D/k}$$

(Assuming initially)
 $x = x_i$ at $t = 0$

⇒ Daniell Grove Model:-

$$\text{Soln.} \rightarrow x^2 + \frac{2D}{K} \cdot x = \frac{2DN_0}{n} (t + \tau)$$

(it will or)

$$t = \frac{x^2}{B} + \frac{x}{(B/A)} - \tau$$

where, $B = A$

$$\tau = \frac{x_i^2}{B} + \frac{x_i}{(B/A)}$$

Here,

$$B = \frac{2DN_0}{n}; \quad A = \frac{2D}{K}$$

- ⇒ A & B depend on depositivity, solubility & oxidising species per unit vol.
- Both are different for different fluid (Wet & Dry)
- τ is the initial time taken for formation of initial oxide by exposure of Si in atmosphere.

* Linear & Parabolic Regimes -

$$x = 0.5 A \left\{ \left[1 + \frac{4B}{A^2} (t+z) \right]^{\frac{1}{2}} - 1 \right\}$$

(Thickness of oxide)

If one starts with thin oxide (or bare Si)

→ Very short time -

$$x = \frac{B}{A} (t+z)$$

$$(t+z) \frac{A^2}{4B}$$

→ Longer time -

$$x^2 = B(t+z)$$

→ Initially faster growth rate, but then slower growth rate, as

Initially it follows Kinetically controlled model,
but later it follows Mass Transfer Control.

* Exponential Regime:

If one starts with Bare oxide,

1. for dry Oxid^n , $z \neq 0$

2. z for thick. 25nm is good fit.

3. Initially, exponential growth.

→ Hypothesis 1 →

1. Charged species form.

2. holes diffuse faster / set up elect. field.

3. Diffusion + Drift \Rightarrow effective diffusivity high.

4. Space charge regime control.

5. length = 15nm for O_2 & 0.5nm for H_2O .

Environment → Wet Oxid^n is not affected.

⇒ Hypothesis 2:

1. In Dry Oxidn, many open areas exist initially.
2. O_2 diffuses fast in Si, hence more initial growth rate.
3. Once covered with SiO_2 , then slow diffus.

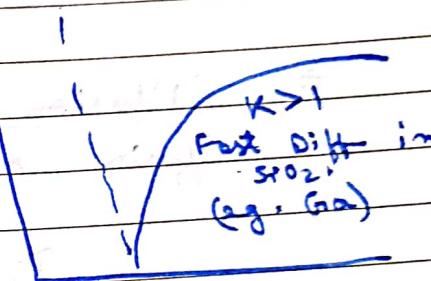
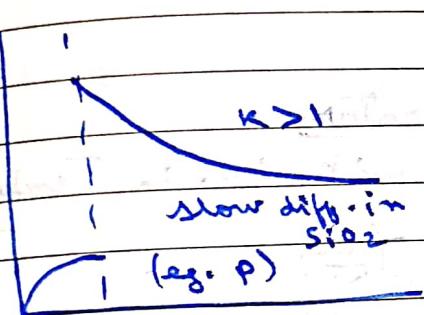
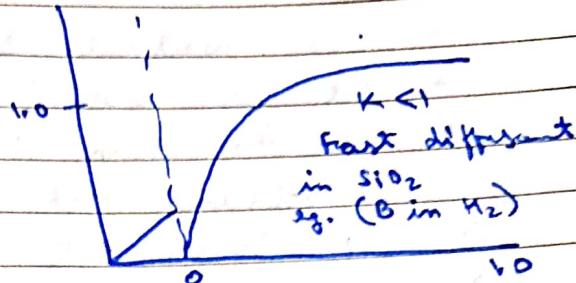
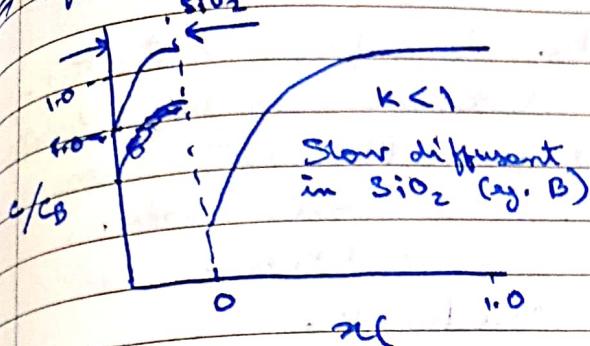
⇒ Hypothesis 3:

1. Even before reaction (at high temp.), oxygen dissolved in Si (reasonable diffusion)
2. Once temp is inc., 5nm quick oxide formation.

⇒ Hypothesis 4:

- 1.

Effect of Doping:



- Doping increases Oxidⁿ rate.
- ex. Boron incorporated in Oxide; more porous Oxide.
- ⇒ More diffusion, parabolic rate const. is higher.
- iii) P not incorp. in Oxide.
- so, no significant change in Parabolic rate constt.

⇒ Issues -

- Na diffuses faster in SiO_2 .
- Uses chlorine during Oxidⁿ. As it,
 1. Helps trap Na.
 2. Helps create volatile comp. of heavy metals.
so, use 3% HCl or Tri-Chlor Ethylene (TCE)

Electrochemical -

- Use neutral soln. & apply potential.
- Pt as counter electrode (hydrogen evolution)
- Use Ammonium Hydrogen Phosphate or Phosphoric Acid or Ammonia soln.
- Si diffuses out & forms Oxide.
- Inc. in Oxide thickness.

⇒ Diffusion & Temperature -

Diffusion co-eff. inc. with inc. in Temp.

$$D = D_0 e^{-\frac{Q_d}{RT}}$$

(Diff. Co-eff.) $\text{m}^2 \text{s}^{-1}$

D_0 → Pre-exp. ($\text{m}^2 \text{s}^{-1}$)

Q_d → Activation energy [J/mol or eV/atom]

R → Gas Constant [$8.314 \text{ J/mol}\cdot\text{K}$]

T → Abs. Temp. [K]

⇒ Non-Steady State Diffusion -

The conc. of diffusing species is a fn. of if both time & position.

$$c = c(x, t)$$

potential.
hydrogen evolution
or
dissolution

Temp.

or $eV/atom$:
 $t - k$

for δf

Sl. No.

Fick's 1st law -
Relates the diffusive flux to the conc. under
the assumption of steady state.
It postulates that the flux goes from
regions of high conc. to regions of low
conc., with a magn. that is proportional
to the conc. gradient (partial derivative)

Fick's 2nd law -

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2}$$

here,

$$c = c(x, t)$$

This law predicts how diffusion causes
the conc. to change with time.

Appln. → Food absorption in body, biopolymers,
population dynamics, s.c. doping.

Sr. No. _____

Sr. No. _____

II) Ion. Implantation-

- Wafer is target in high energy Accelerator
- impurities "Shot" into Wafer.

- Adv.-
- 1. Preferred method of adding Impurities.
 - 2. Wide range of Impurity species
 - 3. Tight Dose Control (\approx few $\mu\text{g/g}$ or 20-30 $\mu\text{g/g}$)
 - 3. Low Temp. Process.

- It is expensive, as it works in vacuum.

- Mathematics involved in equipment -

$$\bar{F} = q_f (\vec{v} \times \vec{B}) \quad (\text{Force on charged part})$$

$$|\vec{B}| = \sqrt{\frac{2mV}{qfr^2}} \quad (\text{Mag. field})$$

$$\text{Implanted Dose, } Q = \frac{1}{nqA} \int_0^T I(t) dt$$

* Electro-Chemical

→ Use neutral solution and apply potential
Pt as counter electrode

* DIFFUSION

Motive is not to produce a layer which is the main objective of oxidation instead is to change the property of the substrate.

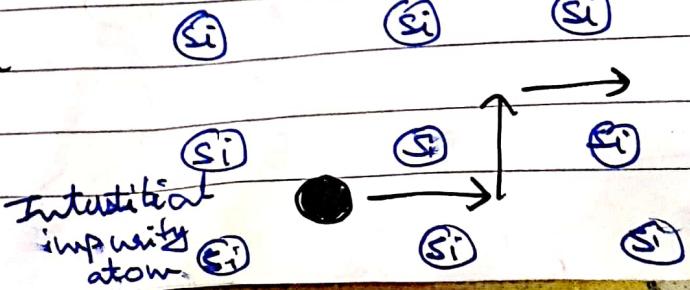
- In oxide, chemical reaction takes place, here no reaction
- Diffusion is the re-distribution of atoms from regions of high concentration of mobile species to regions of low concentration. It occurs at all temperatures, but the diffusivity has an exponential dependence on T
- Pre-deposition: doping often proceeds by an initial predep step to introduce the required dose of dopant into the substrate.

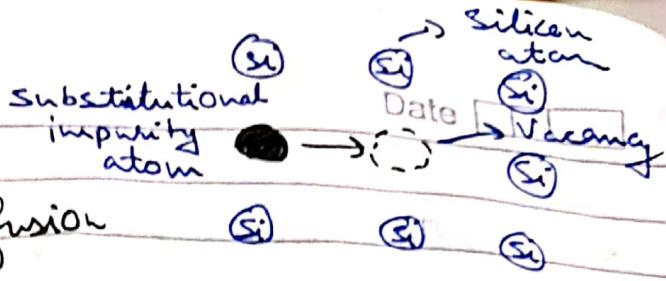
- Drive-In: a subsequent drive-in anneal then re-distributes the dopant giving the required junction depth and surface concentration.

• Diffusion Mechanism in Si

Graph ^{Graph} _{Line}

(a) Interstitial Diffusion
eg - Cu, Fe, Li, H

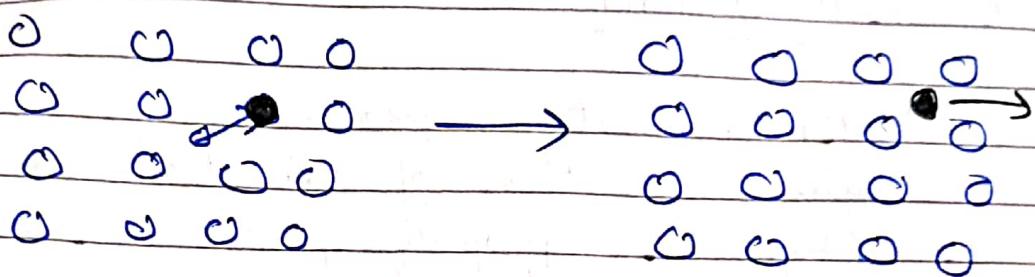




(b) Substitutional Diffusion

e.g. Dopants in Si (e.g. B, P, As, Sb)

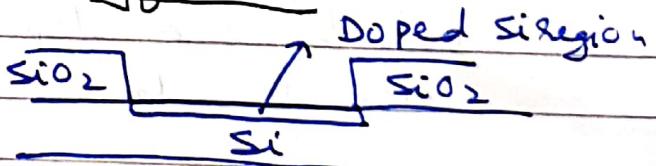
(c) Interstitial Diffusion



In interstitial diffusion an interstitial silicon atom displaces a substitutional impurity during it its an interstitial site where it diffuses some distance before it return to the Substitutional site.

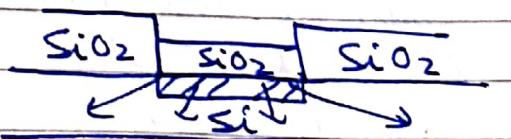
→ Two Step Dopant Diffusion

1) Pre-deposition



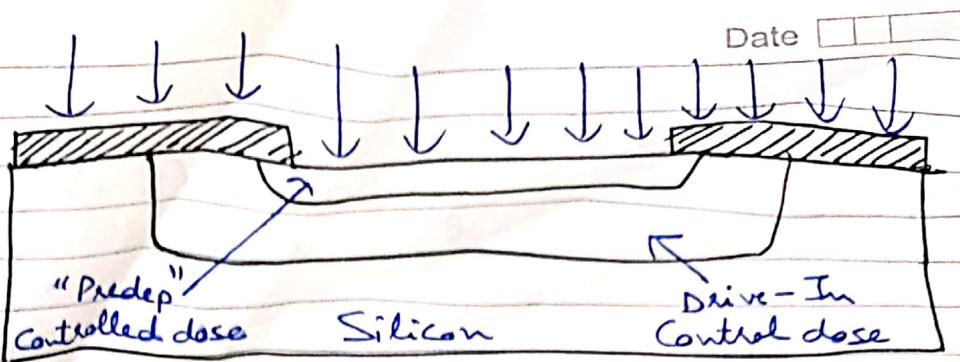
dose control

2) Drive-In



Profile Control
(junction depth)
(concentration)

(Turn off dopant gas
or seal surface with oxide)



Ion Implantation and Annealing

Advantages:-

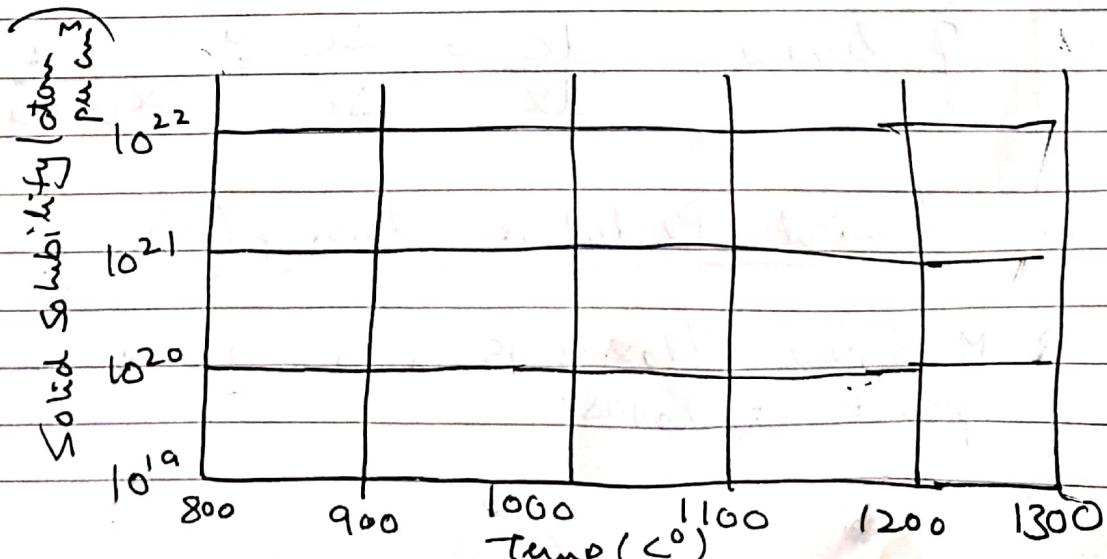
- Room temp mask
- Precise dose control
- $10^{12} - 10^{18}$ atoms μm^{-2} doses
- Accurate depth control

Solid / Gas Phase Diffusion

- No damage created by doping
- Batch fabrication

Problems:-

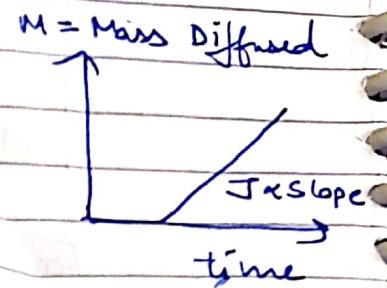
- Implant damage enhances diffusion → Usually limited to solid solubility
- Dislocations: caused by damage may cause junction leakage
- Low surface concentration hard to achieve without a long drive-in.
- Implant channeling may affect profile
- Low dose predeps very difficult.



$J = \text{Flux} = \frac{\text{moles (or mass) diffusing}}{(\text{Surface area}) (\text{time})}$

$$= \frac{\text{mol}}{\text{cm}^2 \text{ s}} \quad \text{or} \quad \frac{\text{kg}}{\text{m}^2 \text{ s}}$$

$M = \text{Mass Diffused}$



$$J = \frac{M}{At} = \frac{I}{A} \frac{dm}{dt}$$

- Steady-State Diffusion

Rate of diffusion independent of time

Flux proportional to concentration gradient = $\frac{dc}{dx}$

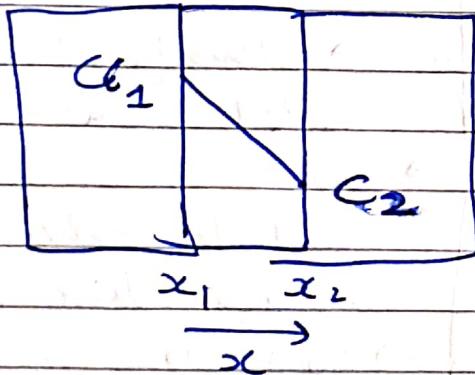


Fig. Fick's first law of diffusion

$$J = -D \frac{dc}{dx}$$

D = diffusion co-efficient

$$\text{If linear, } \frac{dc}{dx} = \frac{\Delta c}{\Delta x} \approx \frac{c_2 - c_1}{x_2 - x_1}$$

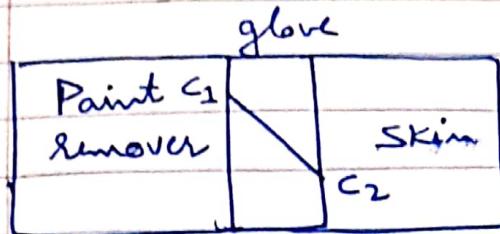
e.g. Chemical Protective Clothing (CPC)

→ Methylene Chloride is a common ingredient of paint removers.

Date

1	2	3
4	5	6
7	8	9
10	11	12
13	14	15

→ If Butyl rubber gloves



$$J = -\frac{D \Delta C}{dx} = -D \frac{C_2 - C_1}{x_2 - x_1} \quad \textcircled{1}$$

$$\text{Data: } D = 110 \times 10^{-8} \text{ cm}^2/\text{s}$$

$$C_1 = 0.44 \text{ g/cm}^3$$

$$C_2 = 0.02 \text{ g/cm}^3$$

$$x_2 - x_1 = 0.04 \text{ cm}$$

After substituting in $\textcircled{1}$

$$J = 1.16 \times 10^{-5} \text{ g/cm}^2\text{s}$$

- Diffusion and Temperature

$$D = D_0 \exp \left[-\frac{Q_d}{RT} \right]$$

D = diffusion coefficient [m^2/s]

D_0 = pre-exponential [m^2/s]

Q_d = activation energy [J/mol or eV/atom]

R = gas constant [$8.314 \text{ J/mol}\cdot\text{K}$]

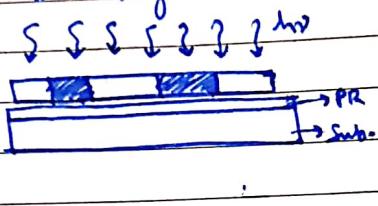
T = absolute temperature [K]

III) Photolithography:

Mask is used to transfer design on the PR layer of device.

It can be done in 3 ways:

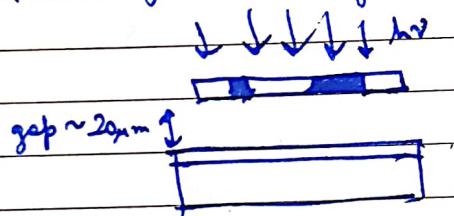
1. Contact Printing -



→ Resolution $< 0.5 \mu\text{m}$

→ The mask plate can be damaged & accumulation defects.

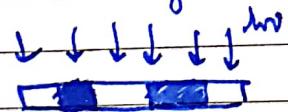
2. Proximity Printing -



$$R \propto (\lambda_g)^{1/2}$$

$\approx 1 \mu\text{m}$ for visible light

3. Projection Printing -



Resolution $\approx 0.2 \mu\text{m}$

→ Optics is complicated & expensive

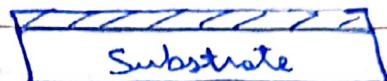
⇒ Photoresists used -

- 1. Neg. PR → Light breaks N-N in light sensitive additive \Rightarrow Crosslink chains.
Sensitive, hard, swelling during develop

IV) Thin Films :

Physical Methods
(Evaporation, Sputtering)

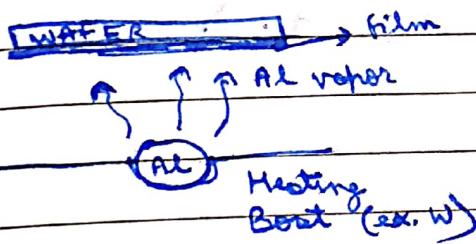
Chemical Methods
(CVD, ALD
Atomic Layer Dep.)



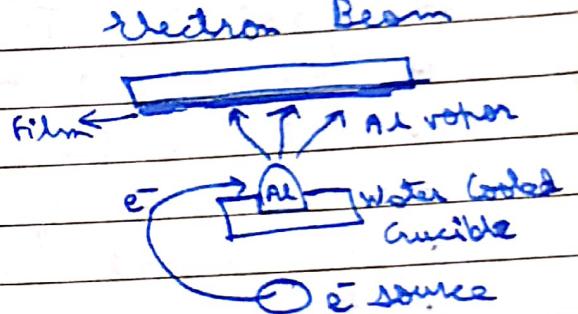
Applications - Metallisation (Al, TiN, W)
Surface Passivation

1. Evaporation -

Thermal

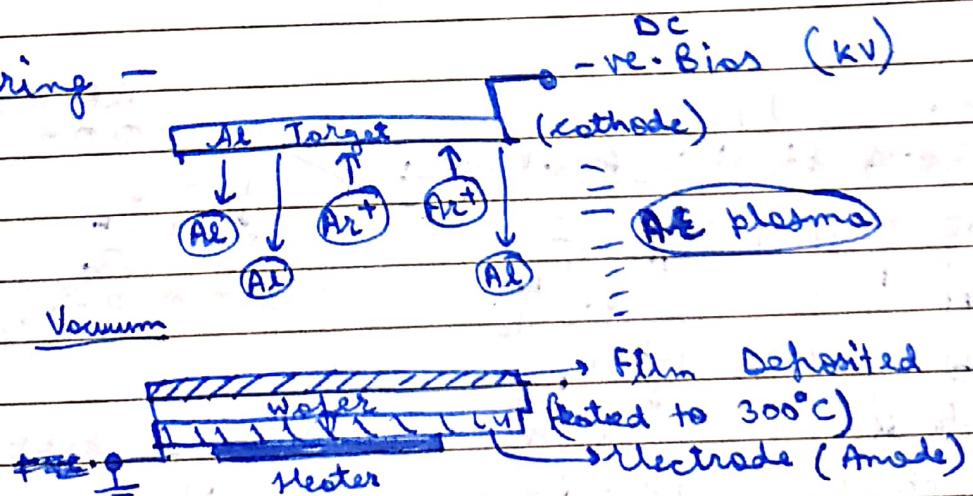


Electron Beam



2. Sputtering -

(a) D.C.

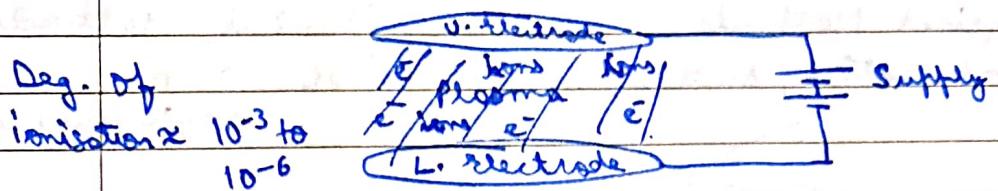


$$\text{Deposition rate} = \text{const.} \times I \times S$$

↓ ↓
Ion Current Spots

- High pressures (1-100 mTorr)
- Used for dep. alloys & compounds.

⇒ Plasma - A low pressure gas where a high energy field is used to drive the ionisation.



Properties -

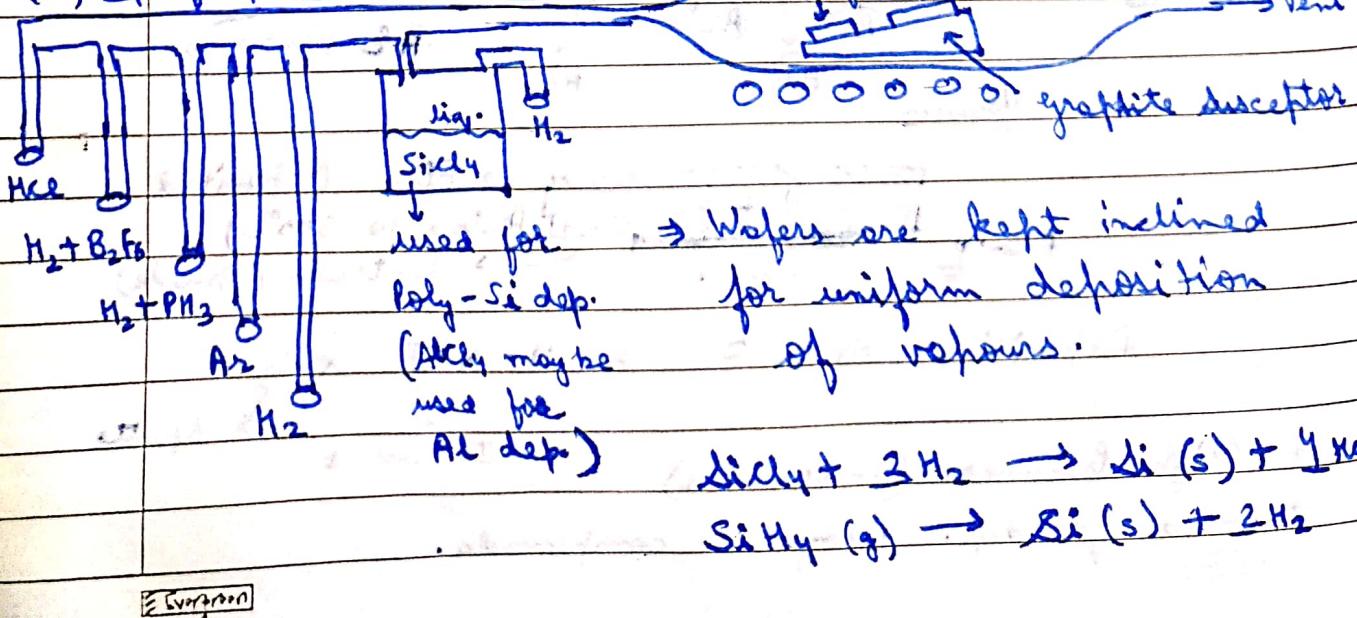
- Contains equal conc. of ions & e.
- Volt. drop is mostly across sheath regions, & const. inside bulk of plasma.
- Weak plasma is used (contains mostly neutral atoms/molecules)

⇒ Desirable Traits of Deposition -

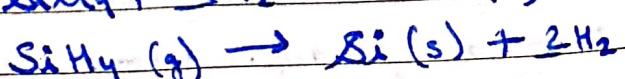
1. low contaminates, good elec. & mech. prop.
2. uniform thickness
3. Conformal growth
4. Planarized films
5. good filling of spaces.

3. CVD -

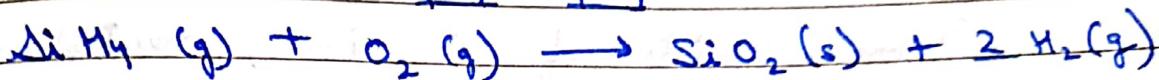
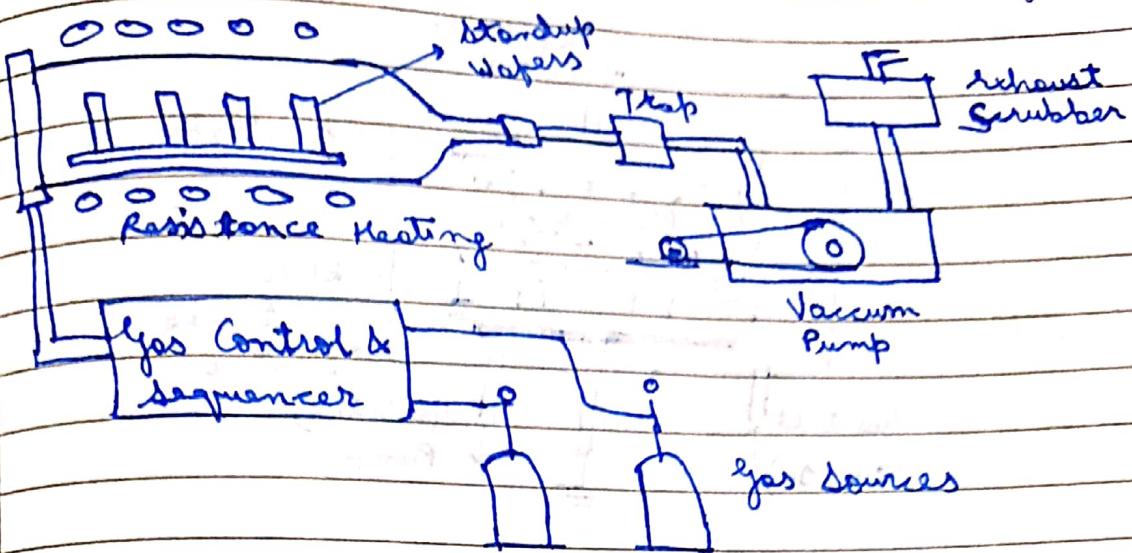
(a) Dep. of epi-Si in Atm. Pressure:



Wafers are kept inclined for uniform deposition of vapours.

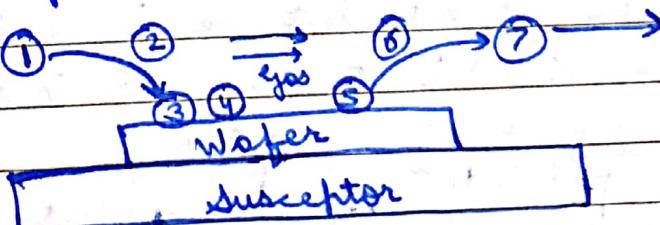


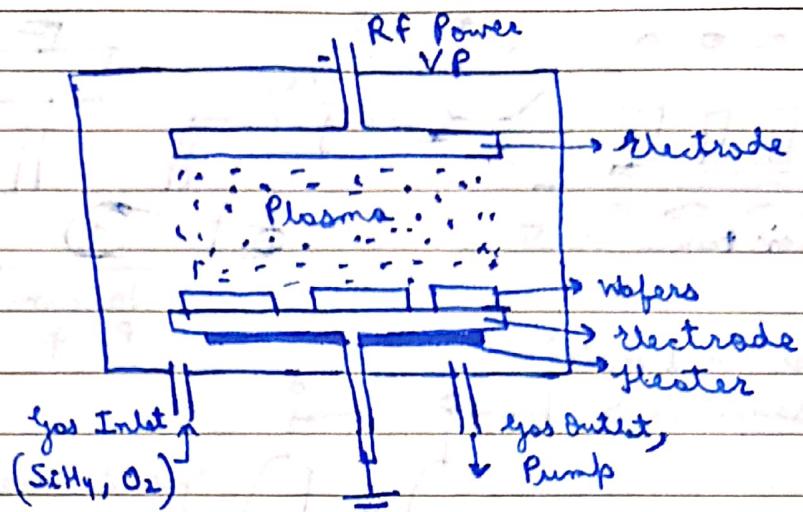
(b) Dep. of amorphous SiO_2 in low Pressure System:-



* Mechanism -

1. Transport of reactants to Dep. region.
2. Transport of react. to the Wafer surface, from main gas stream.
3. Adsorption of reactants on Wafer surface.
4. Surface reactions, incl: chem. decomp. / surface migrations / site incorporations / emission & re-deposition.
5. Desorption of by-products.
6. Transport of by-products through boundary layer.
7. Transport of by-products away from dep. region.



(c) PECVD : (Plasma Enhanced CVD)

Plasma consists of e⁻, ions, neutral mol., excited molecules & free radicals.

Neutral species having incomplete bonding, which are highly reactive (e.g. SiO, SiH₃, F)

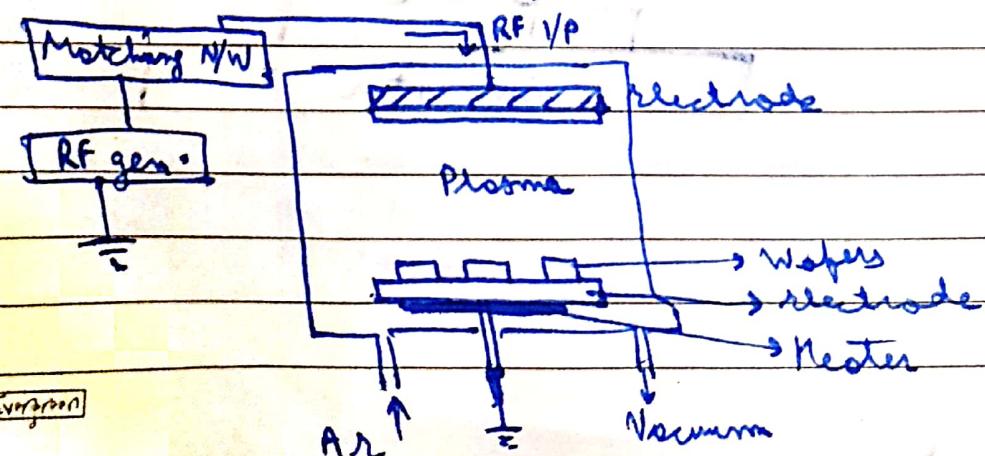
The net result is that surface processes & deposition occur at lower temp. than non-plasma systems.

Adv.: Provides non-thermal energy to enhance processes at lower temps.

2. (b) RF sputtering:

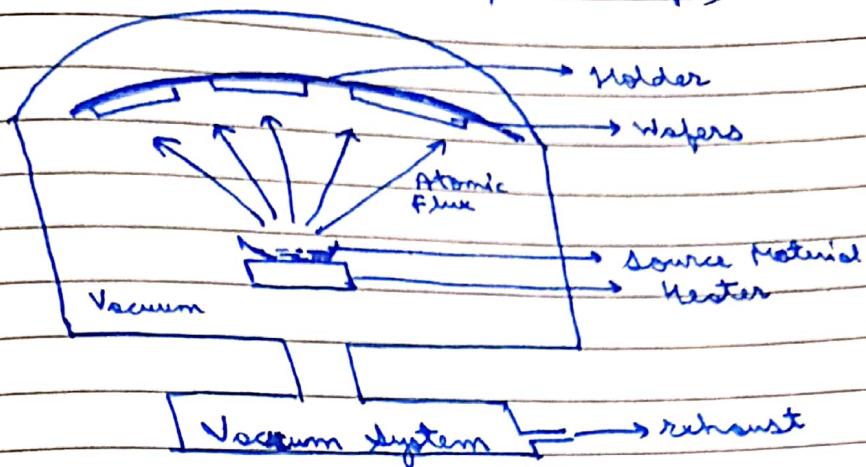
In DC, target electrode is conducting.

For dielectric target, RF is used.



PyD :

(Physical Vapour Dep.)



- uses mainly physical processes to produce reactant species in gas phase to deposit vapours.
- Low Pressure is maintained ($< 10^{-5}$ Torr)
- Deposition rate is determined by emitted flux & geometry of target.

⇒ Adv. of Sputtering over Evaporation:

1. For multi Component thin films, it gives better composition control using compound targets. Resp. depends on pressure of various vapour components & is difficult to control.
2. Better lateral thickness uniformity - superposition of multiple point sources.