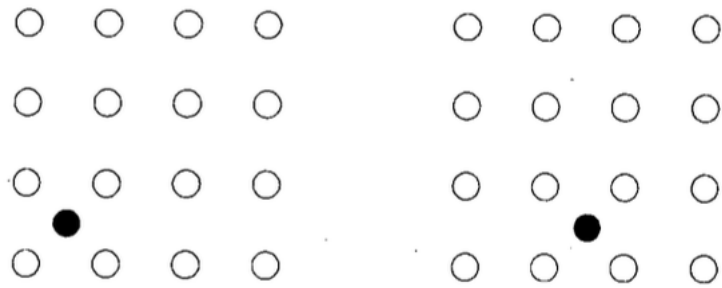


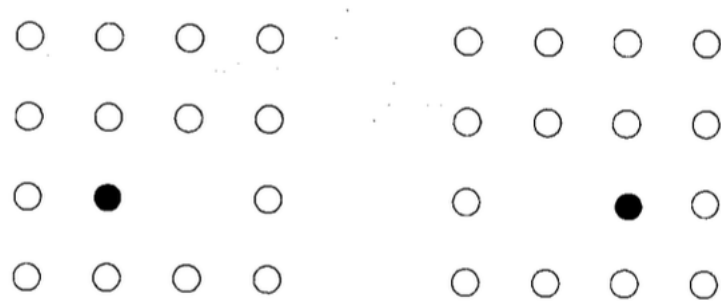
Diffusion

Uses of Diffusion

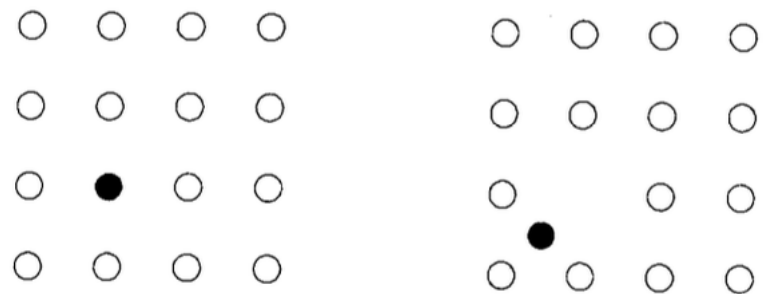
- Diffusion is the most straight forward way to locally dope semiconductors
- Law of diffusion is a well established
- Diffusion is a process by which atoms move in a crystal lattice
- Movement by diffusion is governed by
 - Concentration gradient
 - Temperature
 - Diffusing species
 - Crystal structure, and defect density in the parent media



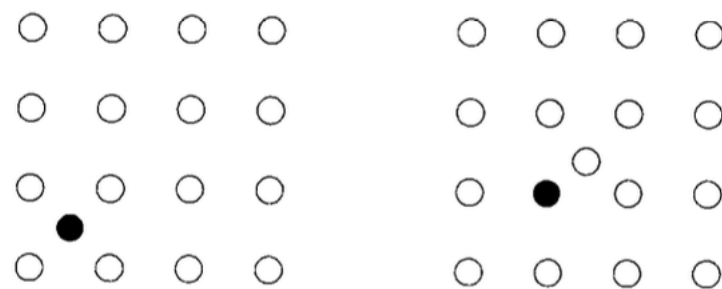
Diffusion by interstitials



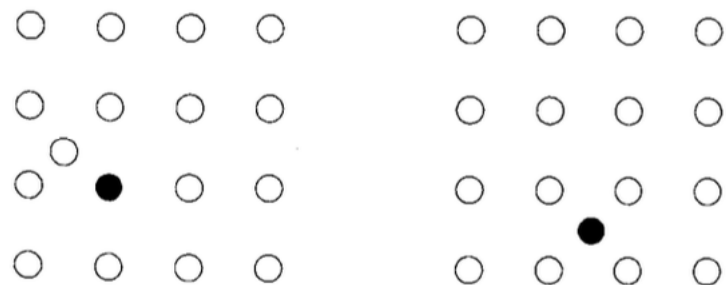
Diffusion by substitution



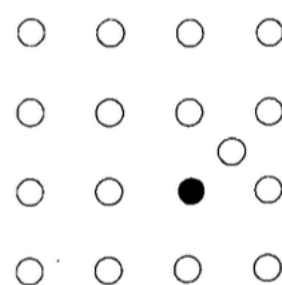
Substitution to interstitials



Interstitial – substitution kick-out

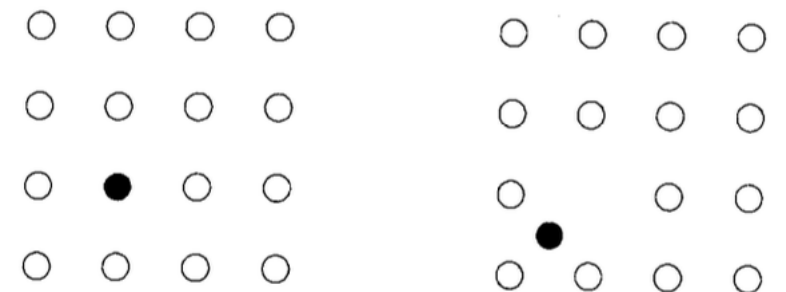
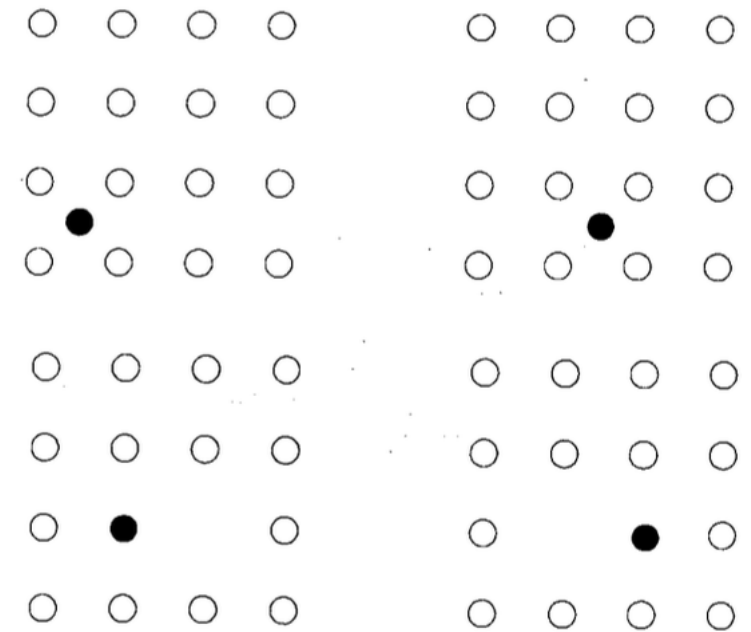


A self-interstitial knocks a substitutional atom to an interstitial position



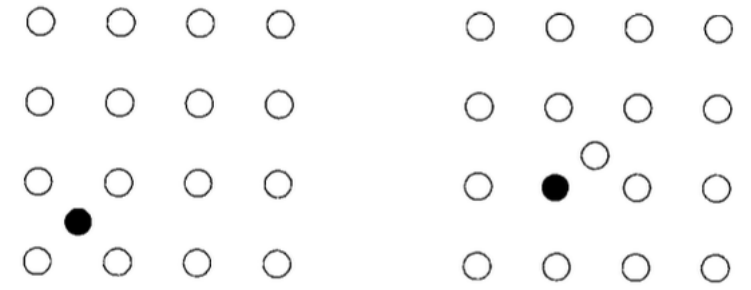
Different types of diffusion

- Interstitials –
 - By far the fastest diffusion method
 - Impurities like Na and Li move in Si like this.
- Substitutional –
 - Typically slow. It requires a near by vacancy for the substitutional atom to move.
 - Or there has to be vacancies that allow for such movements
- Substitutional to interstitial
 - Very fast once in interstitial
 - However, the rate is determined by the vacancy formation rates!
 - Cu and Zn move in Si using this method.



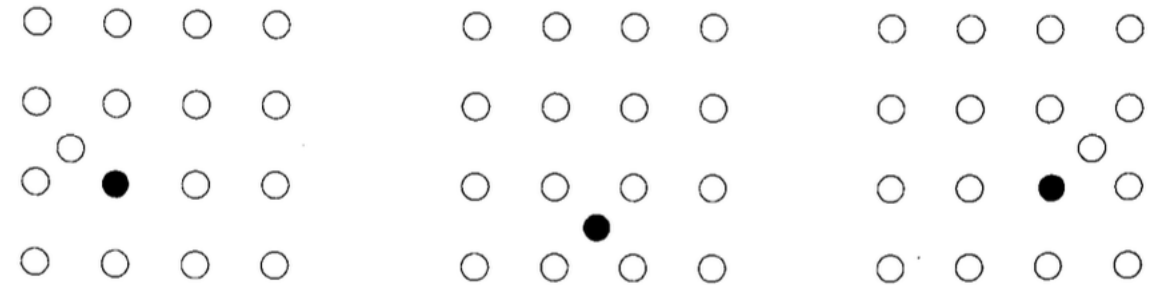
- Kick-out

- Here, a substitutional impurity create a self-interstitial.
- Au and Pt movement in Si is treated in this fashion.



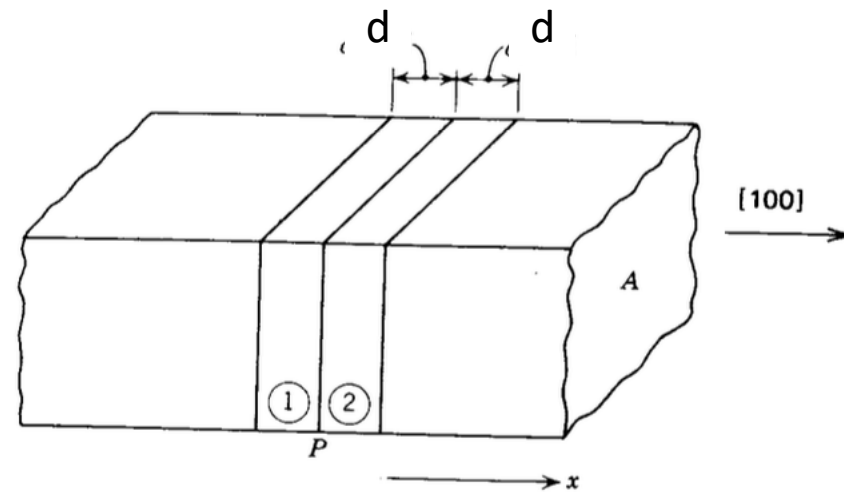
- Substitutional diffusion via interstitial

- Boron and phosphorus move using this



- Other diffusion pathways

- Interchange diffusion
- Grain boundary diffusion
- Combination effects



- Let us take a distance between two interstitials 'd'
- Consider two layers as shown in the figure.
 - If layer 1 has density n_1 and layer 2 has density n_2
 - Net- flow of atoms is $\frac{Ad(n_1 - n_2)}{2}$
 - If we assume the atoms are moving randomly. Half of It will move along the concentration gradient
- Imagine, that once in every 't' seconds, a interstitial can jump from one site to another. Therefore the net flow rate is

$$\frac{\delta n}{\delta t} = \frac{Ad(n_1 - n_2)}{t}$$

- Also remember $\frac{\delta n}{\delta x} = \frac{n_2 - n_1}{d}$

- Therefore, we obtain the equation

$$\frac{\partial n}{\partial t} = \frac{Ad^2}{2t} \left(-\frac{\partial n}{\partial x} \right)$$

$$J = -D \frac{\partial n}{\partial x} \text{ where } D = \frac{d^2}{2t} \text{ (diffusivity)}$$

t is the time taken to jump.

Typically, the atoms in a crystal oscillate at some designated frequencies.
Packets of such oscillations are called as Phonons.

The Debye frequency $\nu_d = \frac{1}{t_d}$ is a cut-off frequency of such oscillations.

$$\nu = \nu_d e^{-\frac{E_b}{kT}}$$

E_b is the energy barrier for such oscillations
T - Temperature

For Si, $\nu_d = 1 \times 10^{13} \text{ hz}$

Non-steady state diffusion

- The concentrations are changing with time.
- There can be some accumulation/depletion in some of the regions

Type equation here.

Consider a section.

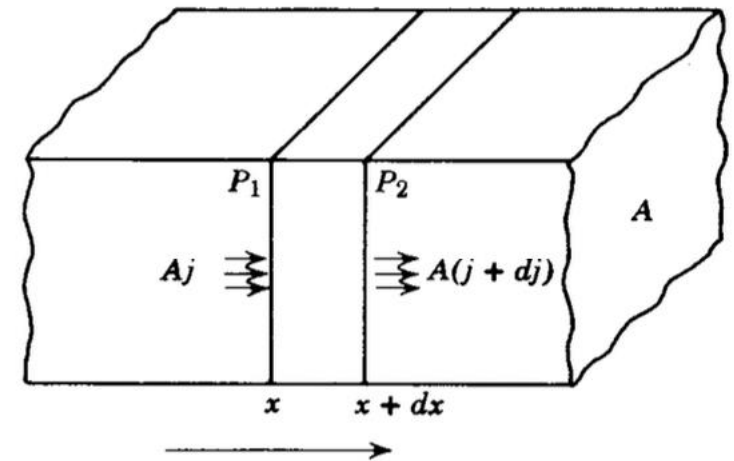
Area – A, width – dx

If the flux density coming in is 'j'

If the outgoing flux is 'j + dx'

Then the change in the density of particles – $-A(j + dj) + Aj = -A dj$

The time dependence of the density change $A dx \frac{\partial N}{\partial t} = -A dj$



$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial N}{\partial x} \right)$$

Fick's second law!

Example of diffusion

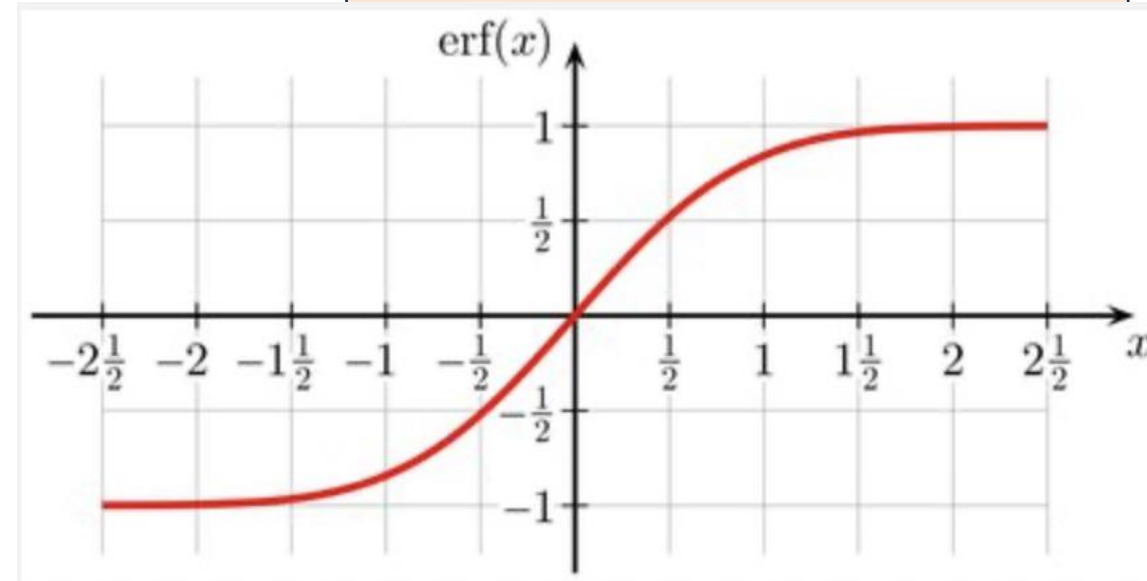
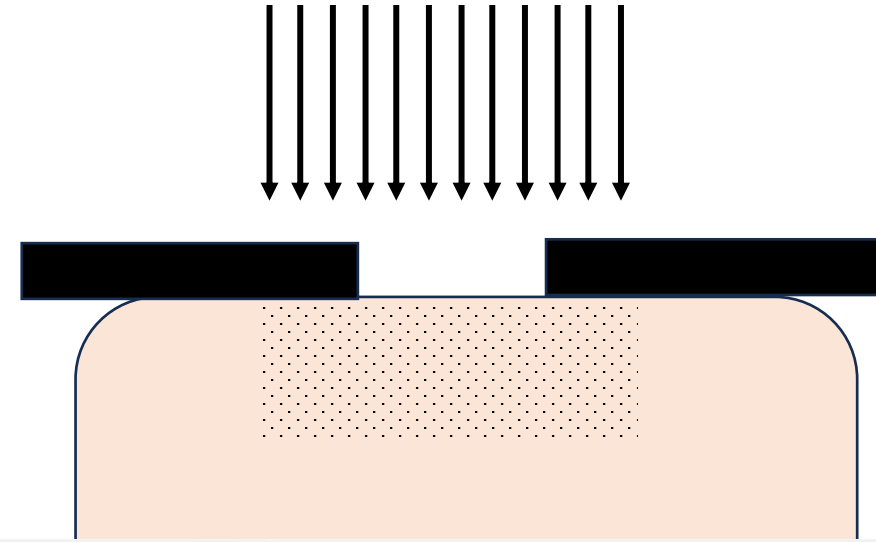
Imagine a situation, where Ar atoms are bombarding the surface.

There are infinitely many atoms at the surface. And the concentration is not going to change with time.

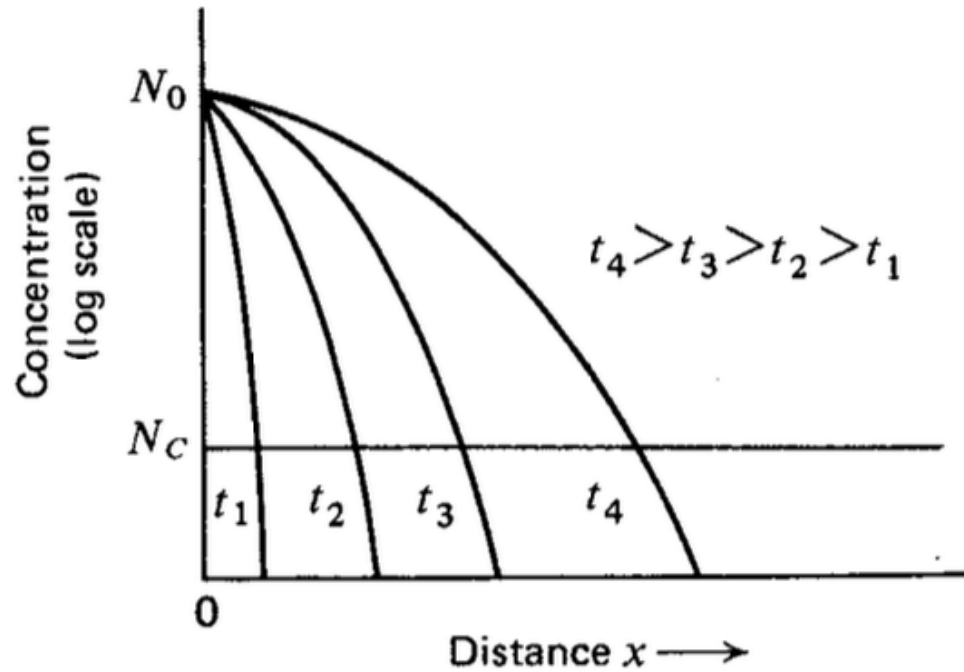
This gives us a boundary condition. The equation can now be solved.

$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial N}{\partial x} \right)$$

$$N(x, t) = N_0 \operatorname{erfc} \frac{x}{2\sqrt{Dt}}$$

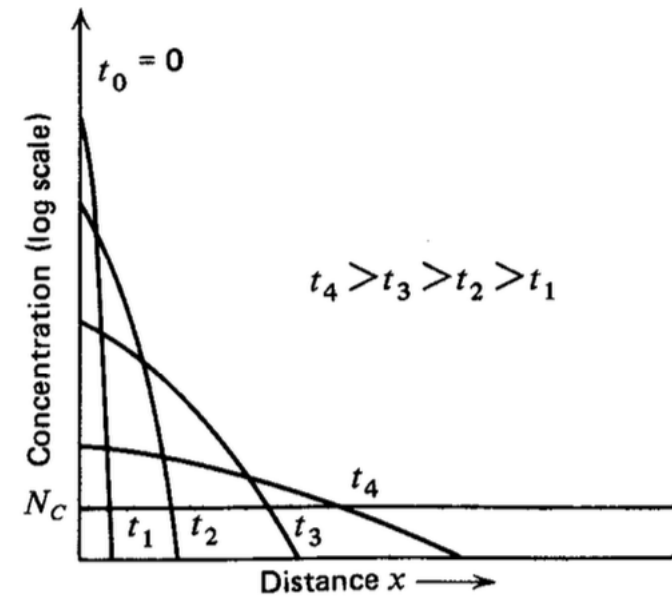


Drive-in diffusion

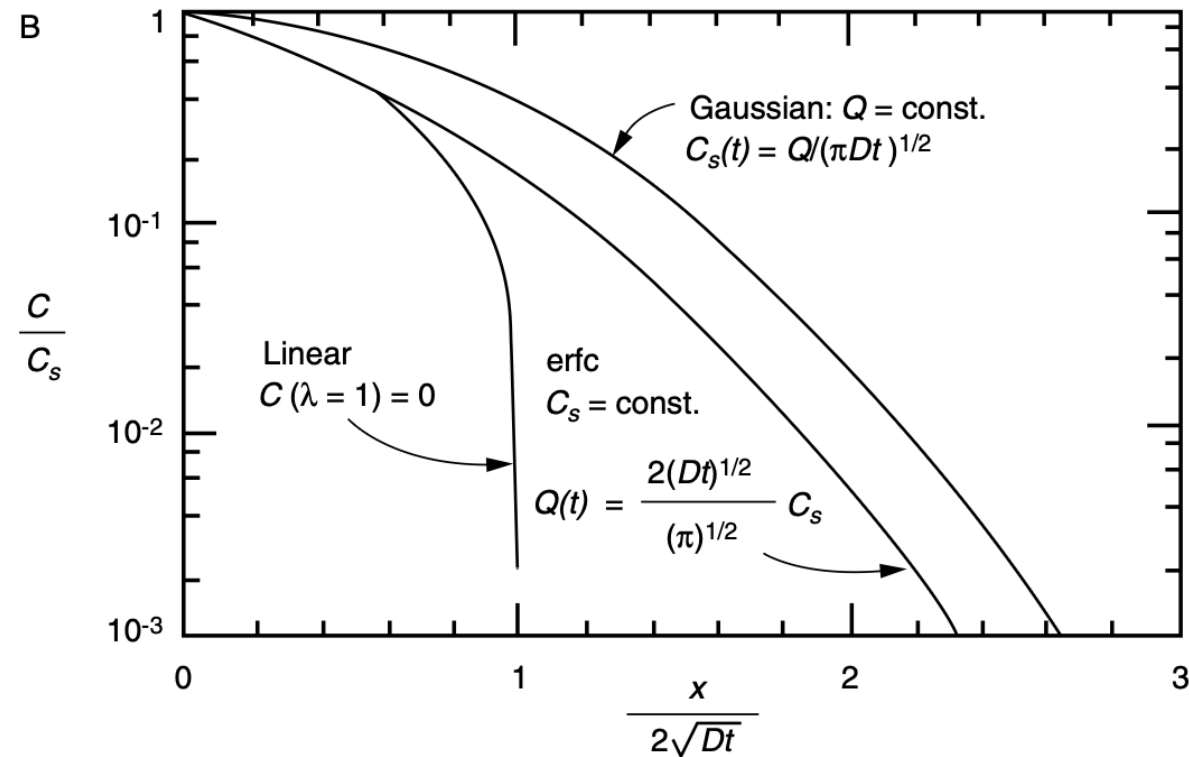
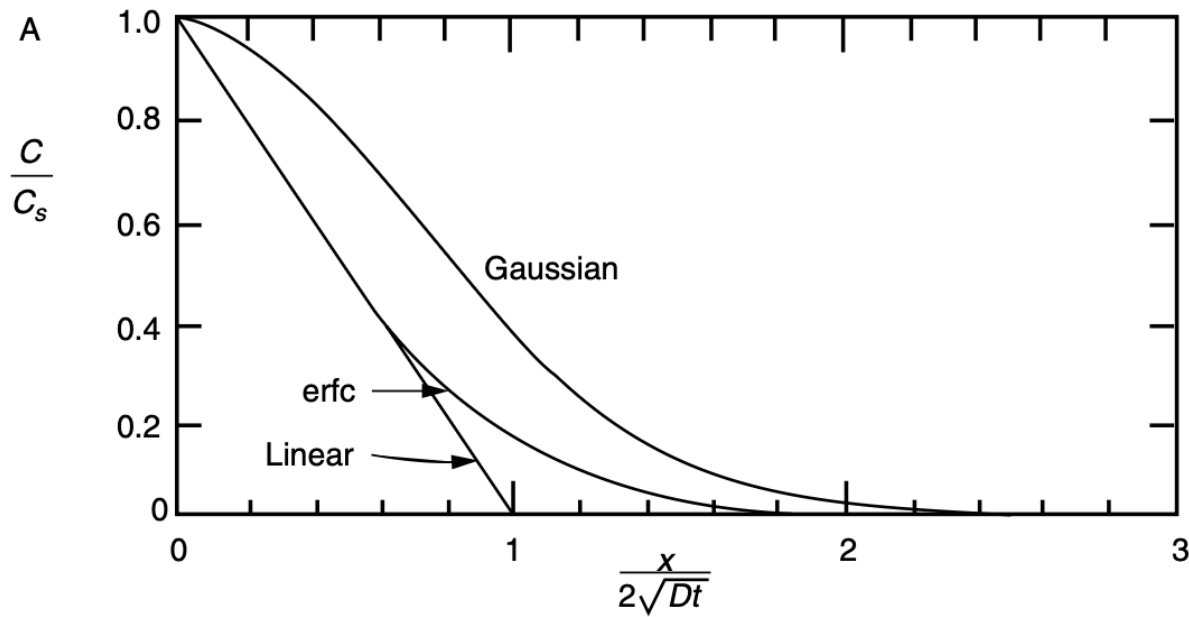


Impurity concentration as a function of time.

$$N(x, t) = N_0 \operatorname{erfc} \frac{x}{2\sqrt{Dt}}$$



$$N(x, t) = \frac{N_0}{\sqrt{\pi Dt}} e^{-\left(\frac{x}{2\sqrt{Dt}}\right)^2}$$



Depth profile of dopants

There always exists a diffusion distance

$$\lambda = 2\sqrt{Dt}$$

Characteristic diffusion length.

Upto about 0.6λ , a linear profile works very well.

The total number of dopant diffused is given by

$$Q = \int_0^\infty N_0 \operatorname{erfc} \frac{x}{2\sqrt{Dt}} dx = \frac{2\sqrt{Dt}}{\sqrt{\pi}} N_0$$

When you have a drive-in diffusion,

The surface concentration goes as $N(t) = \frac{Q}{\sqrt{\pi Dt}}$

D – Dopant diffusivity (strong function of the dominant diffusion scheme).

$$D = D_0(T_0) E^{-\frac{E_a}{kT}}$$

E_a – Activation Energy (typically 0.5 – 1.5 eV)

D at 1100C is about $2 \times 10^{-13} \frac{cm^2}{s}$ for phosphorus

$\lambda = p\sqrt{Dt}$ where $p = 0.87 - 1.6$ depending on the material system.

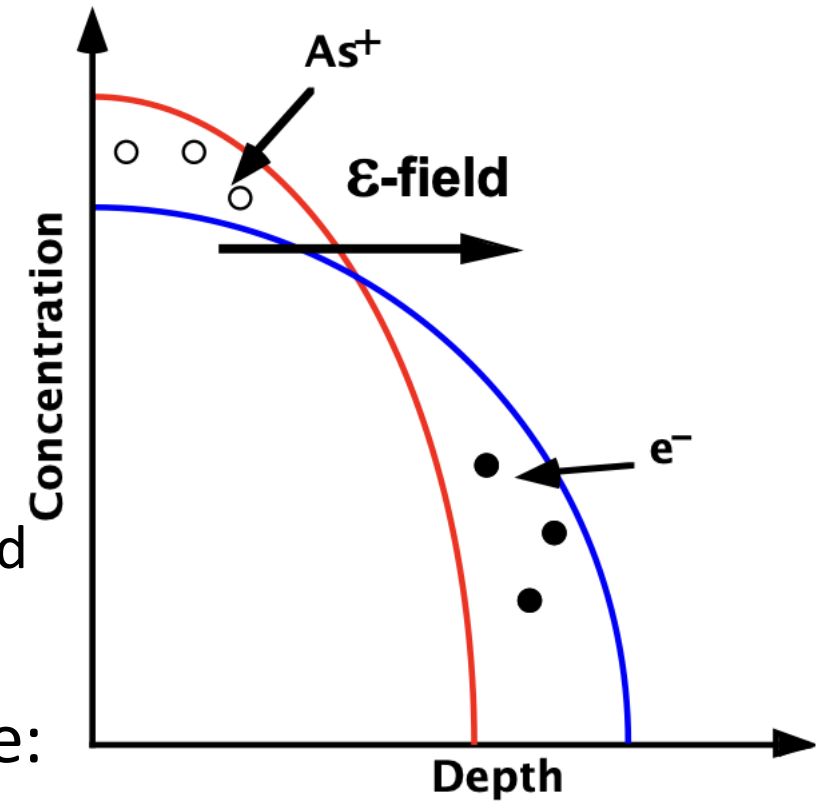
Impurities under electric field

- For eg: If As is diffusing a medium
 - The excess electrons diffuses faster!
 - This leads to ionized As atoms. Leading to an electric field
- If there exists an electric field E
- An impurity atom with valance z experiences a force:

$$F = zeE$$

However, if there is no damping, the impurity atoms will accelerate to infinite velocity!

$$F = ZeE = m_d \frac{dv}{dt} + \alpha v$$



If there exists a diffusing flux

$$J = -D \frac{\partial N}{\partial x}$$

An additional velocity $v = \mu E$ is implied on the diffusing atoms.

$$J = -D \frac{\partial N}{\partial x} + N\mu E$$

If we employ the Einstein's equation $D = \frac{kT}{q} \mu$

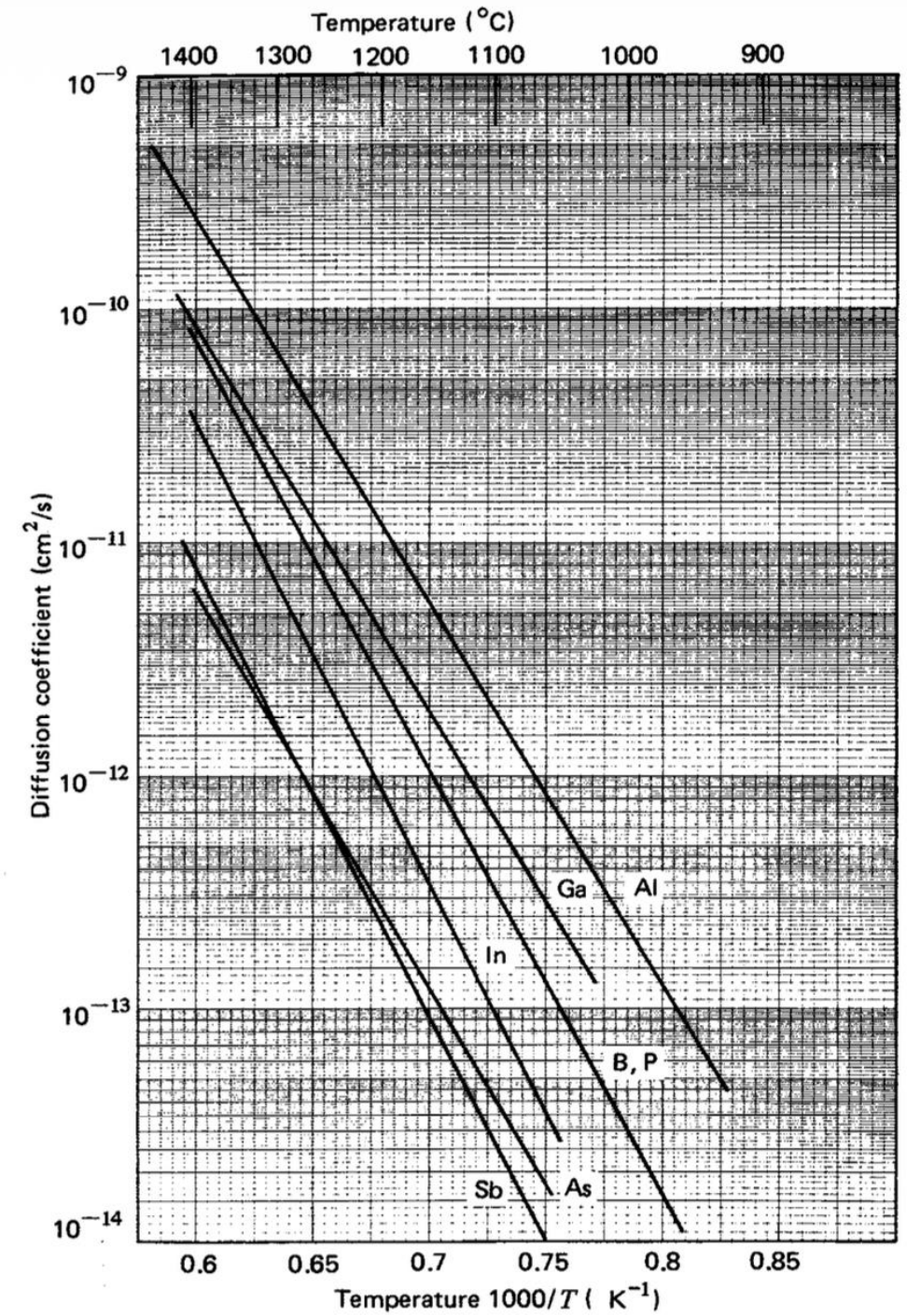
$$J = -D \left[\frac{\partial N}{\partial x} + \frac{NqE}{kT} \right]$$

Typical diffusing species in Si have a strong temperature dependence

As – Low misfit strains, low diffusivity, abrupt junctions

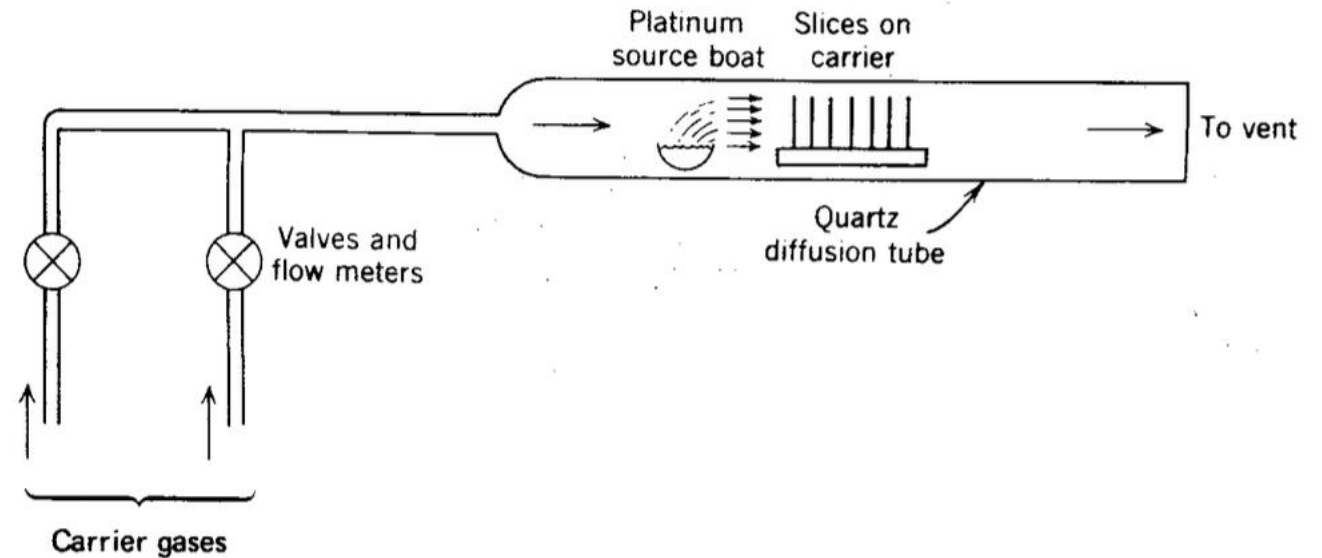
B – Large strains, Low solid solubility, high diffusivity,

P – high solubility and high diffusivity (Normally used in contacts)



Diffusion Methodologies

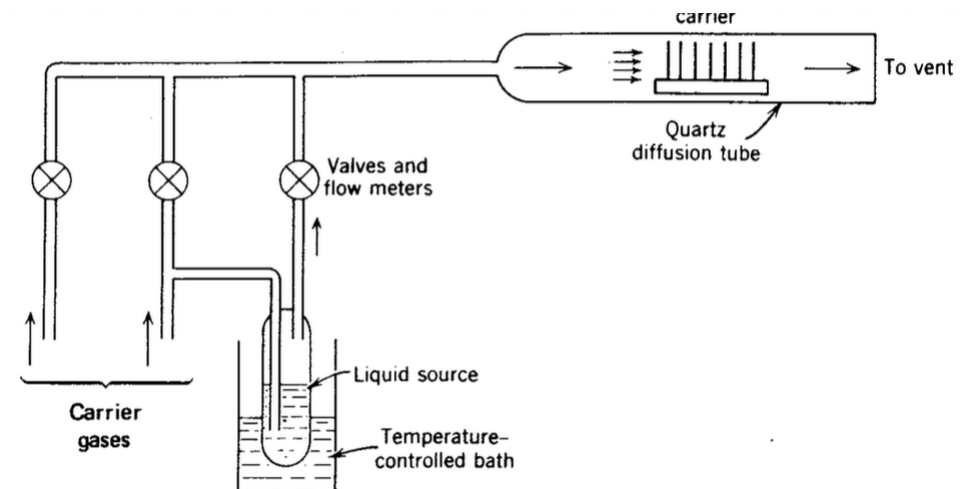
- Depending on vapor pressures of solid sources
- A carrier gas carries the dopant atoms in the vapor phase
- In some cases, a multi-zone furnace is needed
- Problem: Heavy metal contamination from the boats employed.



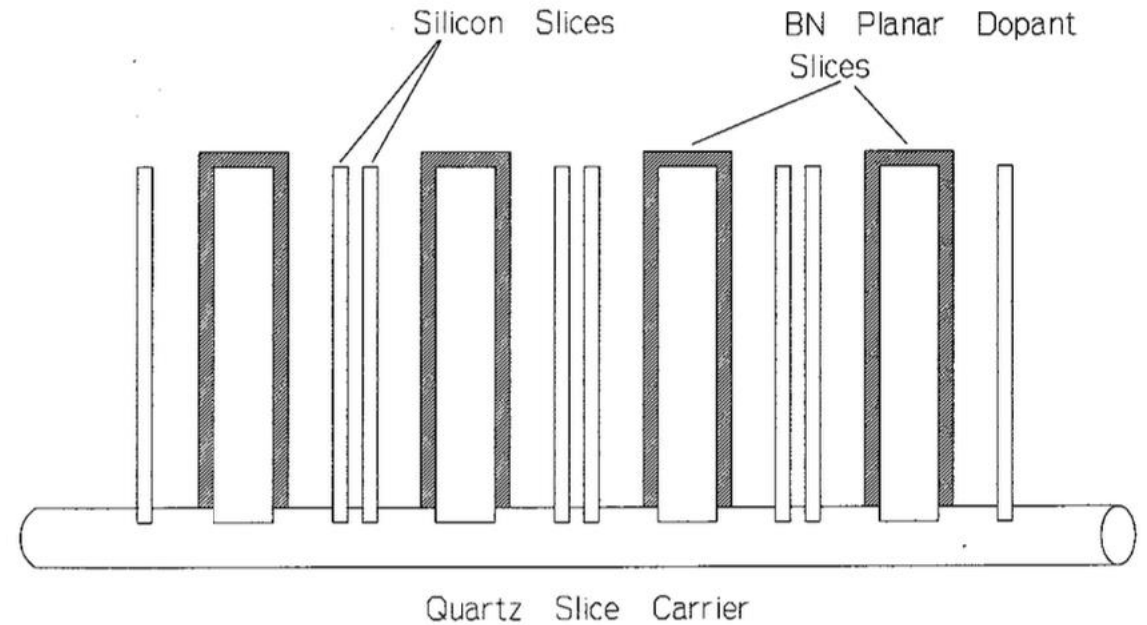
The dopants can be bubbled.

Liquid sources are available that can be carried.

Precise control on the dopant concentration
Less contamination.



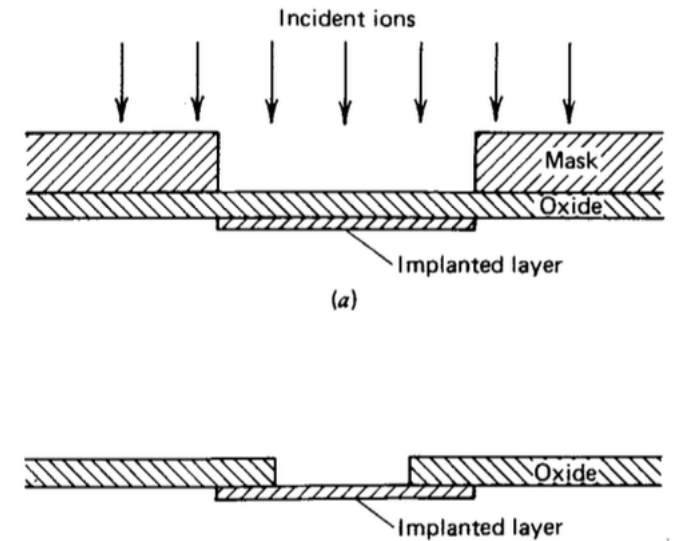
- By far, the simplest:
 - No special gasses are required.
 - Uniform vapor transport.



Parameters	Boron	P	As	Au
Diffusivity [m^2/s]	10^{-12}	$\sim 10^{-12}$	$\sim 10^{-13}$	10^{-10}
Misfit	0.254	0.068	0.035	
Carrier density achievable cm^{-2}	5×10^{19}	3×10^{20}	2×10^{21}	

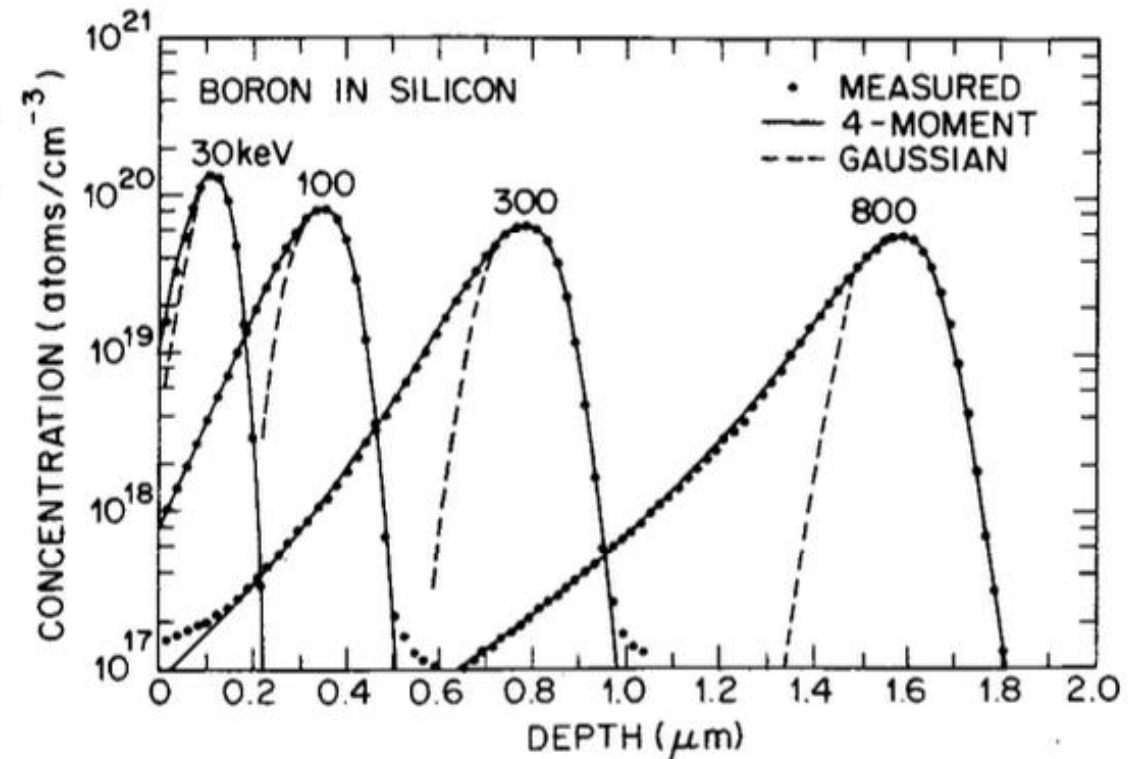
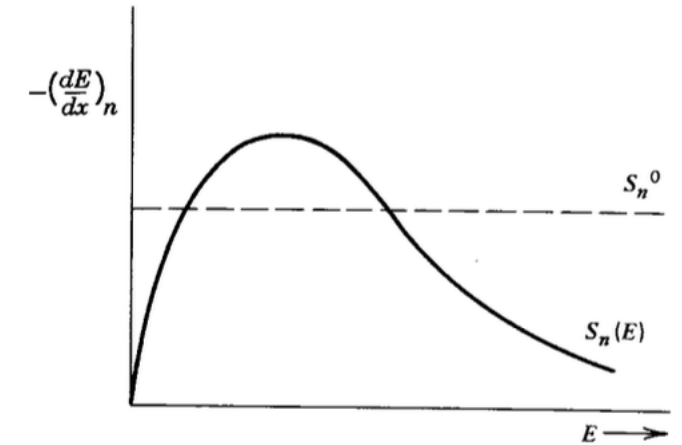
Ion Implantation

- Current technologies centers on this method
 - A mass selective ion beam
 - A wide range of dosage ($10^{11} - 10^{17}$ ions/cm) with 1% resolution.
 - Room temperature implantation.
 - Independent control on dose and depth profile
 - Dopant to the excess of dopant solubility.

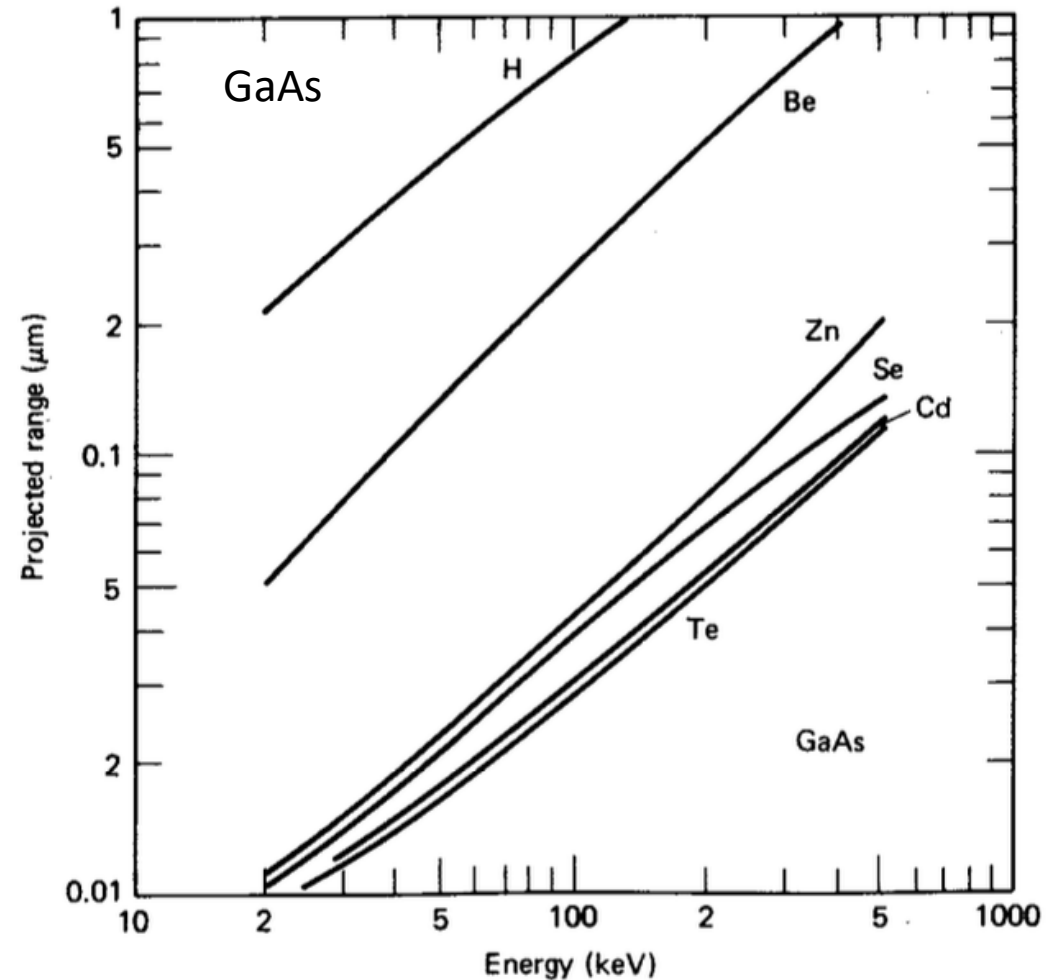
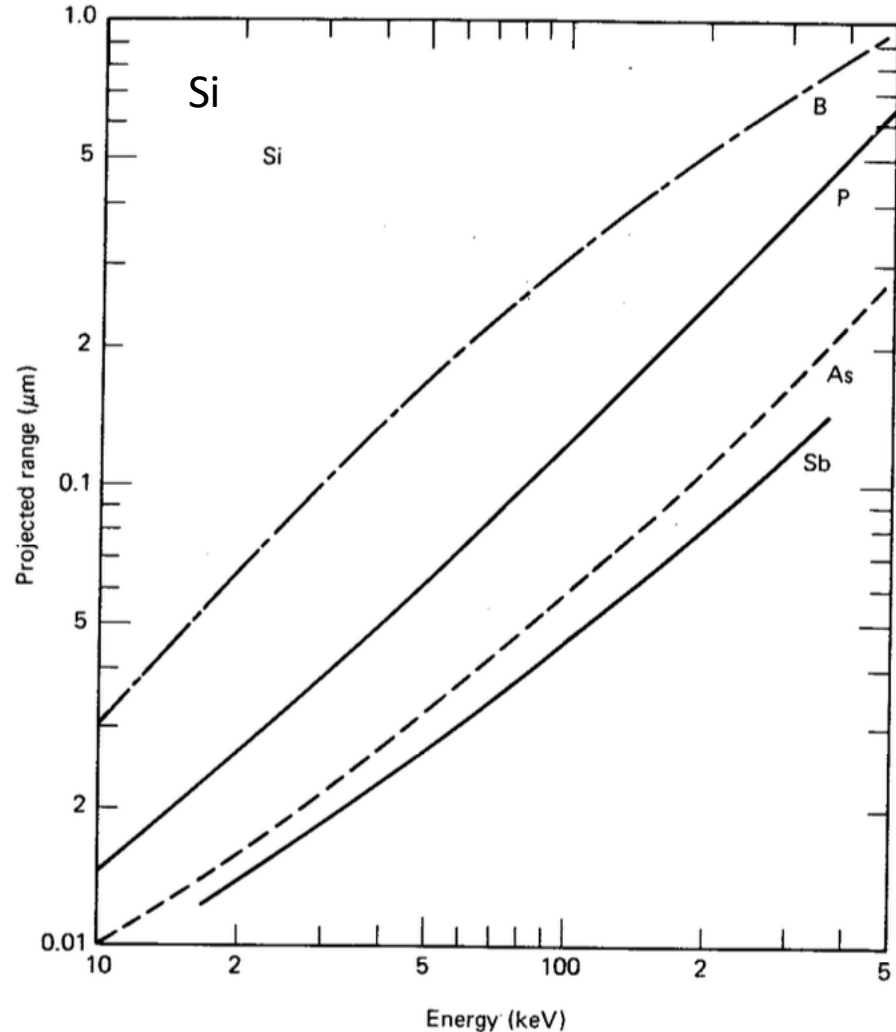


Excited Ion pathway

- The accelerated ion can be stopped in the medium either by the substrate nucleus
 - The rate of energy loss of the ion is low at high energies
 - At moderate energies, it loses more energy
 - An averaged value is about 10 – 200eV/A
- An additional electronic stopping is also relevant.
 - The electrons interact inelastically by excitation processes.

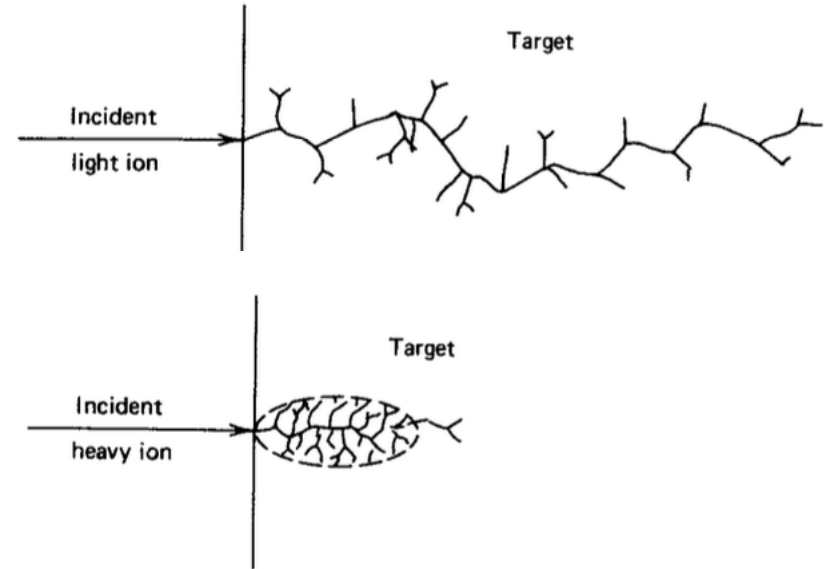


Projected Ranges of Dopants

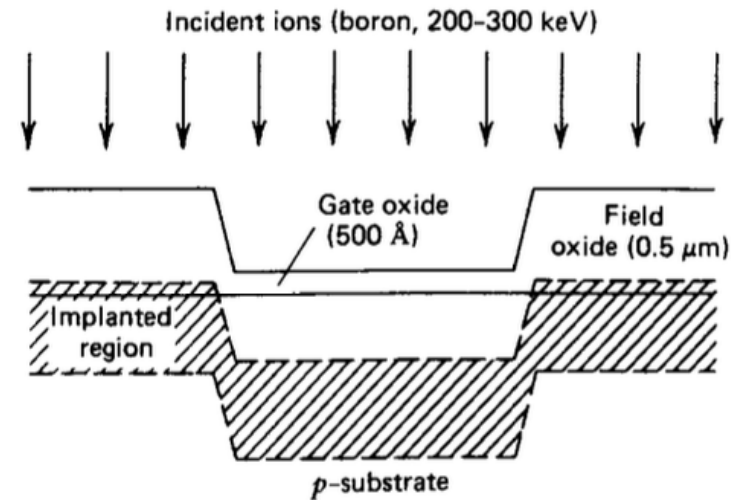
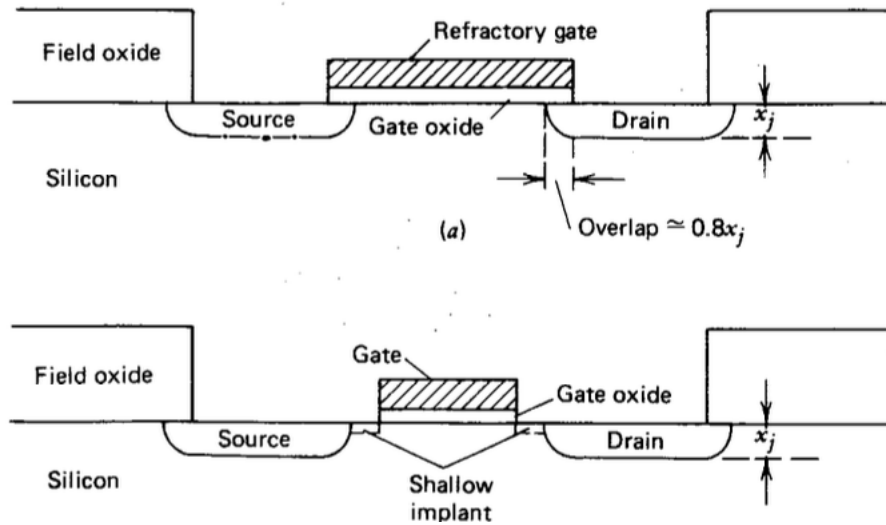


Implantation Damage

- Ion implantation leads to excessive damage.
- Large density of Frankel defects, bivacancies and dislocations are formed.
- Amorphous regions are formed.
- Solution:
 - Annealing of the semiconductor
 - Si is typically annealed at 1200 C
 - GaAs annealed above 500 C
 - Typically duration of about 15 – 30 mins

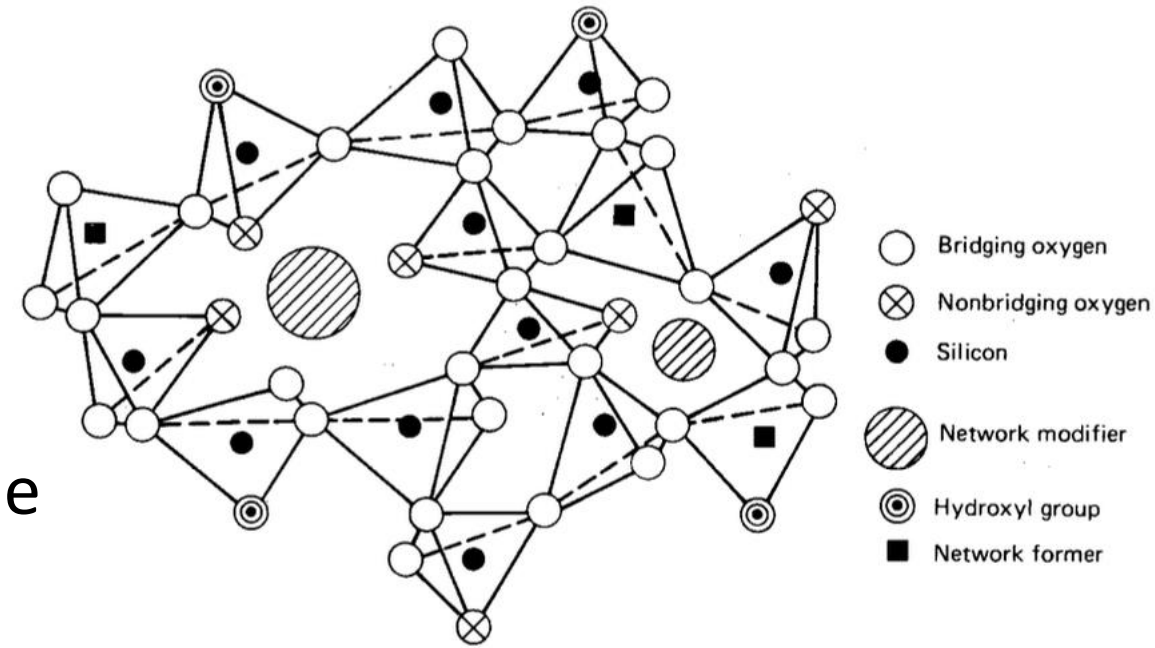


Examples of device fabrication



Thermal Oxidation

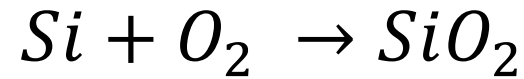
- Any freshly cleaved surface has 15-20Å oxide
- SiO₂ melts at 1732 °C
- The amorphous SiO₂ (Fused Silica) is unstable below 1710.
- A crystallization de-vitrification happens below 1710 C.
- However, the rate of this is very slow below 1000C
- Extrinsic SiO₂
 - SiO₂ with impurities
 - B/P can replace some of the Si atoms - called network formers
 - They leads to charged impurities
 - Interstitial impurities like Na, K – Called network modifiers



Oxide Formation

- Si Oxidation proceeds through oxidation species diffusing into the Si substrate.
- The oxide layer itself acts as the diffusion barrier
- The reaction rate is ever decreasing with thickness
- The diffusion is the rate controlling step for
 - When oxidation species is O_2 (called dry oxidation) with thickness greater than 40 Å
 - When the oxidation species is H_2O (called wet oxidation) with thickness greater than 1000Å.

- Dry oxidation:



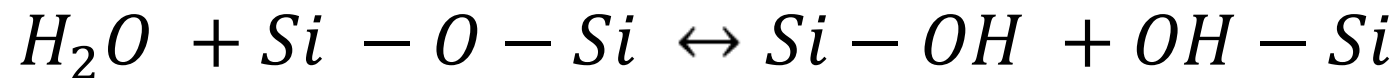
One molecule of oxygen leads to one molecule of SiO₂.

- Wet oxidation:

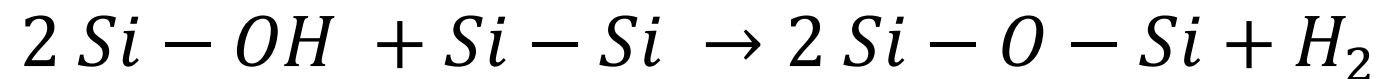


Two molecules of water is required for one molecule of SiO₂

The process is a bit more complex.

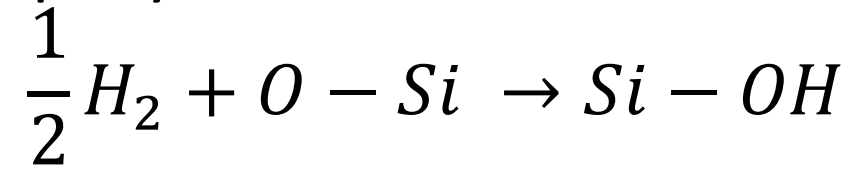


(weakened Silica structure)



The hydroxyl ions react with the Si interface.

- Hydrogen diffuses rapidly



This leads to weakened Silica structure.

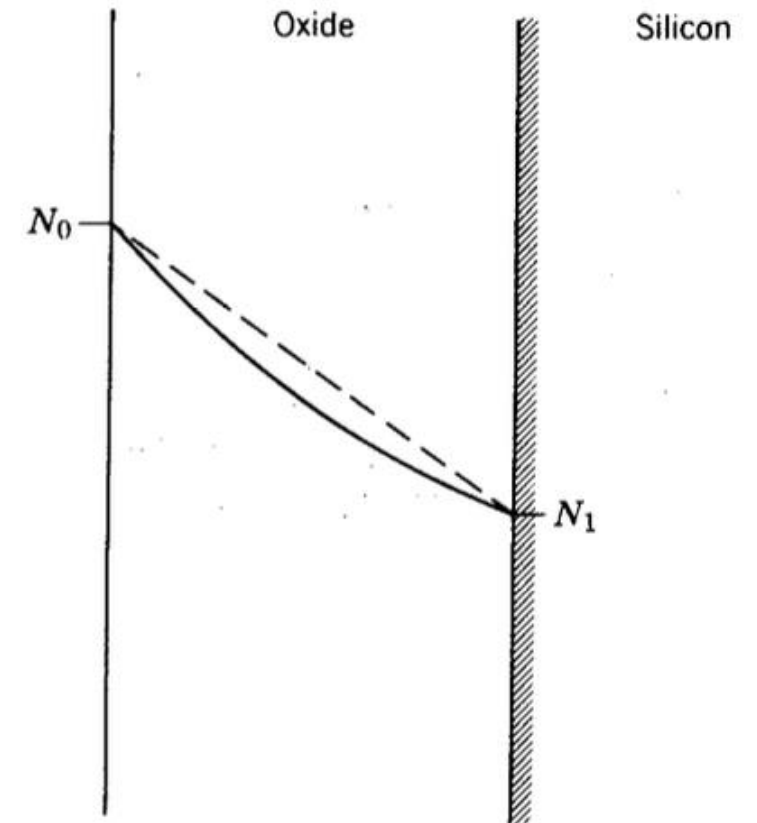
Imagine, a state where a slab of Si was taken.

At any time 't', some thickness 'x' of SiO₂ is grown.

There are some oxidizing species in the gas phase (O₂ or H₂O) .

If their density is N_0 at the surface, a steady state diffusion can occur that leads to a concentration of the species N_1 at the surface.

$$J = -D \frac{\partial N}{\partial x} = -D \frac{[N_0 - N_1]}{x}$$



- To maintain a steady state concentration at Silicon surface, the reaction rate must equal the current of the oxidizing species.

$$\text{Therefore } j = KN_1$$

- Substituting we get

$$J = \frac{DN_0}{x + \frac{D}{K}}$$

The rate of growth of oxide in time dt - $J * \frac{dt}{n} = dx$

Therefore we now write $\frac{dx}{dt} = \frac{J}{n} = \frac{\frac{DN_0}{x + \frac{D}{k}}}{n}$

Integrating once gives: $x^2 + \frac{2D}{k}x - \frac{2DN_0}{n}t = 0$

$$x = \sqrt{\left(\frac{2N_0D}{n}t\right)}$$

Oxidation rates

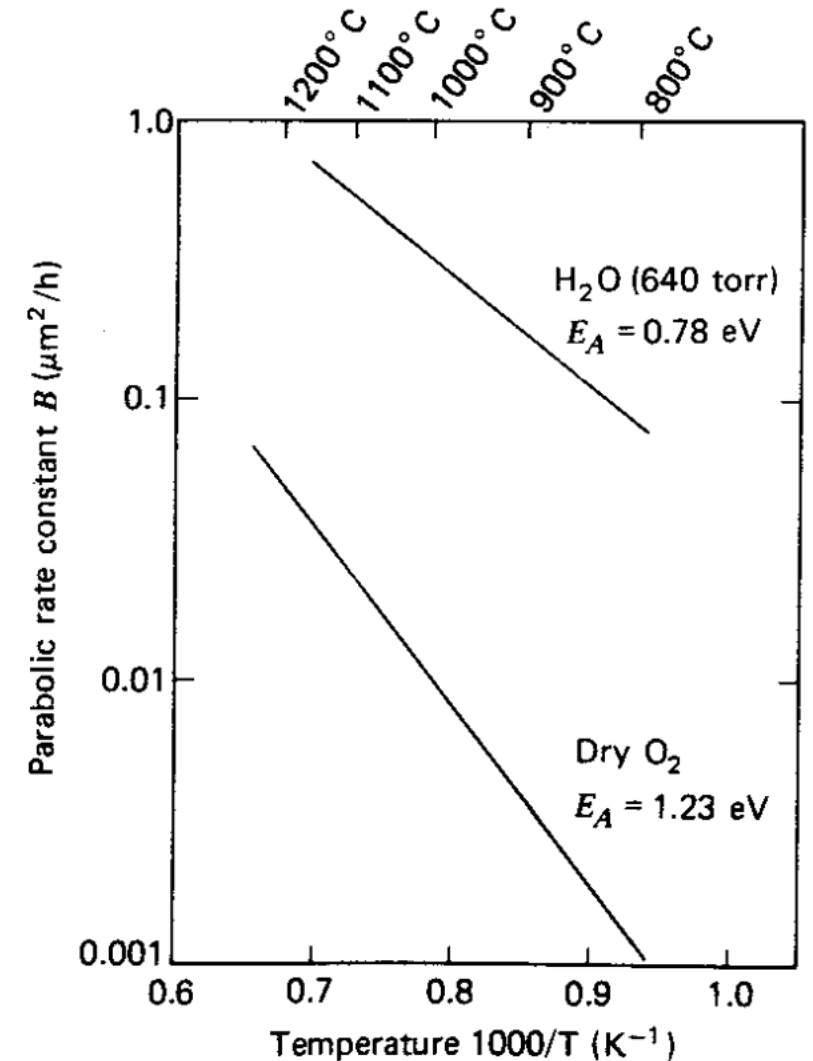
- Generally, the rates are described as

$$x = \sqrt{Bt}$$

For small times, the rates look linear.

Therefore, B is called as parabolic rate constant.

At all temperatures the wet oxidation is much faster than dry oxidation



Properties of interest for oxide

- Diffusion and Masking properties

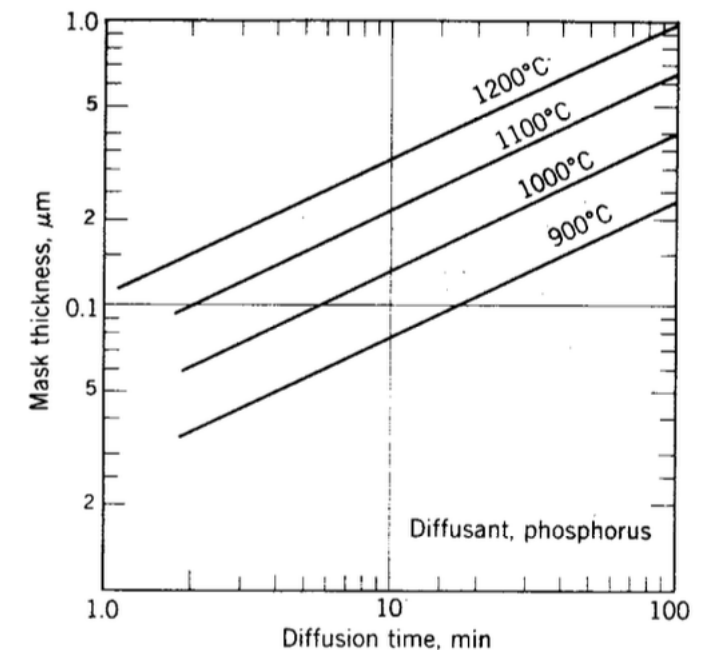
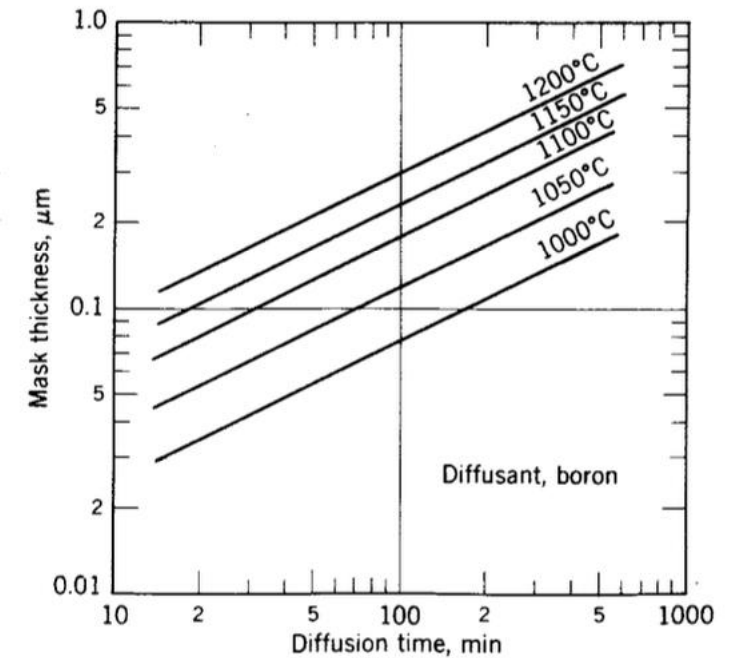
Oxide is used as a diffusion barrier for fabrication.

The properties of the barrier depends on the ability to form networks

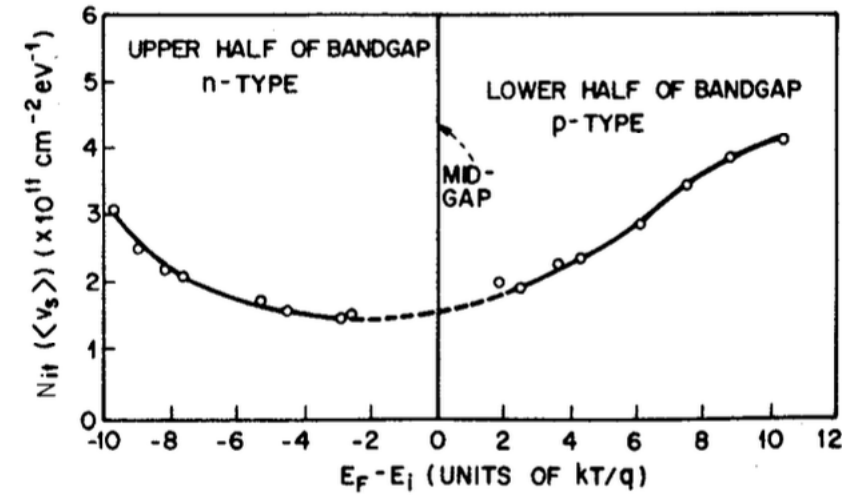
Boron and phosphorous forms B_2O_3 and P_2O_5 glasses that are very stable. Forming excellent masks.

The mask size increases as diffusion time increases.

Mask requirement for Boron is higher than that of Phosphorous.



Electronic Properties of oxides



- Mid-Gap charge states
 - Breaking periodicity at the SiO_2/Si interface leads to mid-band gap states
 - Termed Tamm/Shockley-states are due to broken covalent bonds
 - Freshly cleaved surface has at least 10^{15} cm^{-2}
 - Fast traps are shallow ($< 1 \mu\text{s}$)
 - Slow traps are deep ($> 1 \mu\text{s}$)
 - Wet-hydrogen treatment can passivate shallow
 - High temperature oxidation process can help slower traps.

Recombination and Other effects

- Deep-level trap sites act as recombination centers
- Reduce lifetime.
- Recombination velocity is proportional to density of interface traps
- Hot-electron effects:
 - The barrier for an electron in Si conduction band to SiO₂ band is 3.2 eV
 - While high enough, large device biases can accelerate electrons
 - Electrons get trapped when they get “hot”