Lecture#6:

Diffusion

Diffusion

Diffusion

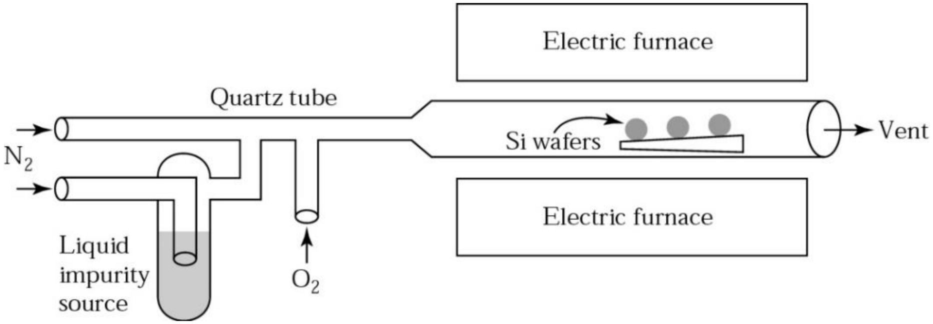
- Diffusion has been **the primary method of introducing impurities** such as boron, phosphorus, and antimony into silicon.

Purpose

- Impurity control -> resistivity
- Majority carrier type
- Majority carrier concentration
- Diffusion depth

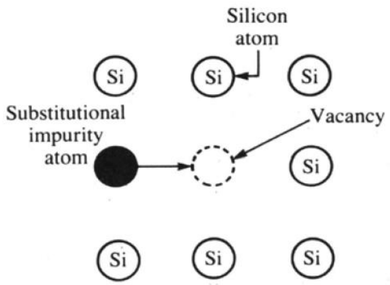
Process

- 1. Deposition of a high concentration of the desired impurity
- 2. At high temperature (900 to 1200 °C), the impurity atoms move from the surface into the silicon crystal



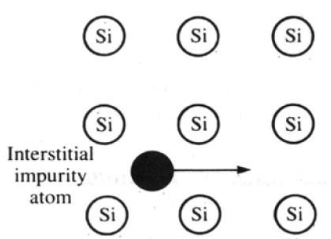
Diffusion

Substitutional or vacancy diffusion



- The impurity atom "substitutes" for a silicon atom in the lattice.
- Vacancies must be present in the silicon lattice statistically.

Interstitial diffusion



- The impurity atom, called an interstitial, can jump form one interstitial site to the next interstitial site.
- Interstitial diffusion proceeds much more rapidly than substitutional diffusion.

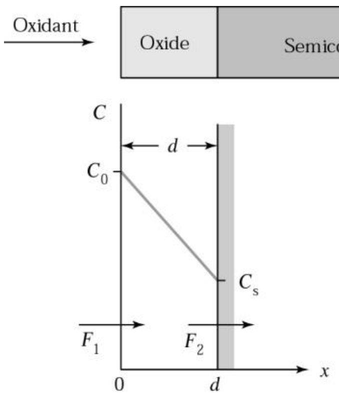
Substitutional diffusion	Interstitial diffusion
Need vacancy supply	Diffusion without vacancy
Slow diffusion	Rapid diffusion
Good process control	Need activation*

* Impurity atoms needs to occupy substitutional site in the lattice in order to be act as donors or acceptors

Diffusion

Fick's law of diffusion

- the particle flow per unit area, *F* (particle flux), is directly proportional to the concentration gradient of the particle:

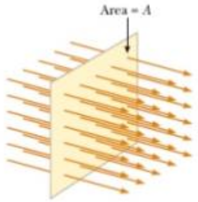


(equilibrium, steady state)

$$F = -D\frac{\partial C}{\partial x}$$ *Fick's 1st law*

where D is the diffusion coefficient and C is the particle concentration.

$$\text{Flux} = \frac{\text{Num Change of atom}}{\text{Unit A x Unit time}}$$



(one-dimensional continuity equation)

$$\frac{\text{Flux}}{\text{Unit L (x)}} = \frac{\text{Num Change of atom}}{\text{Unit A x Unit time x Unit L(x)}}$$

$$\frac{\partial F}{\partial x} = \frac{\boxed{\dfrac{\text{Num Change of atom}}{\text{Unit V}}}}{\text{x Unit time}}$$

Concentration

$$\rightarrow \frac{\partial C}{\partial t}$$

(low concentration of dopant atoms)

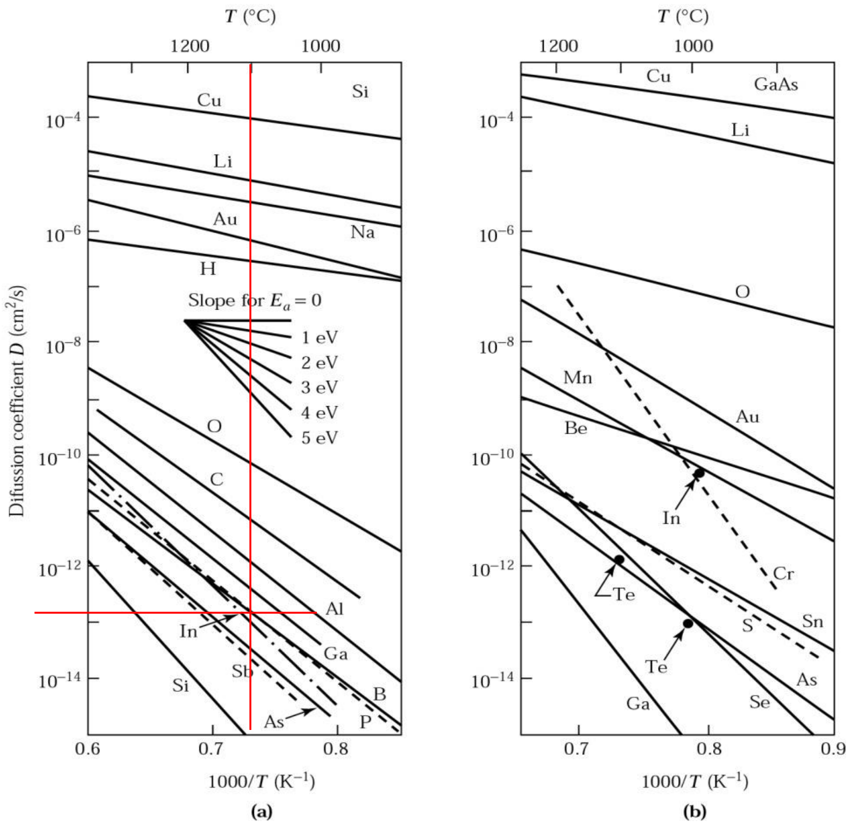
$$-\frac{\partial F}{\partial x} = \frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) = D\frac{\partial^2 C}{\partial x^2}$$

Fick's diffusion equation (Fick's 2nd law)
: Fick's second law predicts how diffusion causes the concentration to change with time.

Diffusion coefficient

$$D = D_0 \exp\left(\frac{-E_a}{kT}\right)$$

Slope (Ea) = activation energy



Diffusion coefficient as a function of the reciprocal of temperature for (a) silicon and (b) gallium arsenide (for low concentration)

Element	D_0 (cm²/sec)	E_a (eV)
B	10.5	3.69
Al	8.0	3.47
Ga	3.60	3.51
In	16.5	3.90
P	10.5	3.69
As	0.32	3.56
Sb	5.60	3.95

Diffusion coefficient of B in silicon at 1100℃ ?

$D = D_0 \exp\left(\frac{-E_a}{kT}\right)$ = 10.5exp (- 3.69/(8.617x10^{-5}x1373))

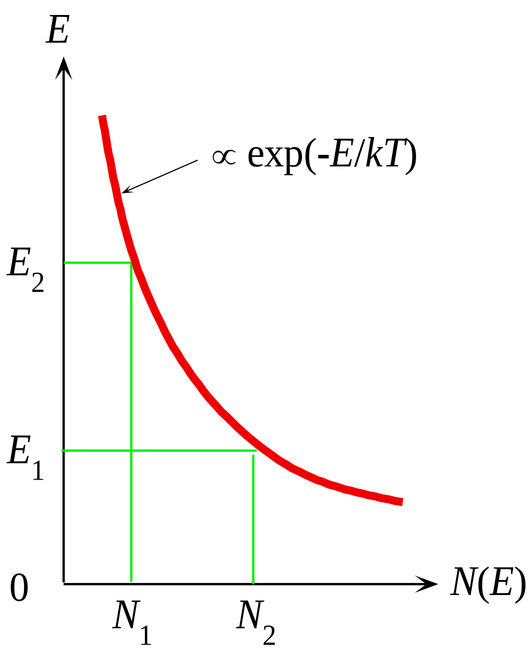
= 2.96 x10^{-13} cm²/sec

Values of k[1]	Units
1.380 648 52(79) × 10^{-23}	J·K^{-1}
8.617 3303(50) × 10^{-5}	eV·K^{-1}
1.380 648 52(79) × 10^{-16}	erg·K^{-1}

[Note] Boltzman Classical Statistics

Diffusion

- **Boltzman energy distribution**



- In statistical mechanics and mathematics, a Boltzmann distribution is a probability distribution, probability measure, or frequency distribution of particles in a system over various possible states.

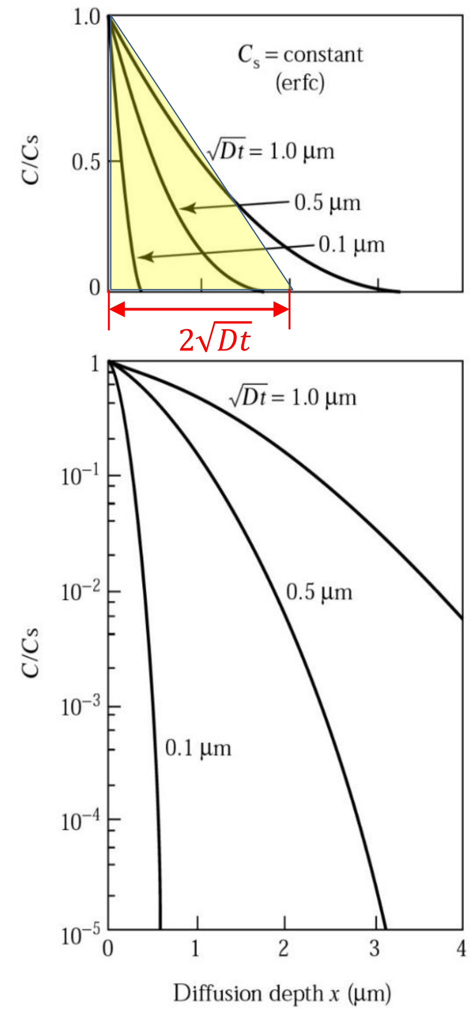
The Boltzmann energy distribution describes the statistics of particles, e.g. electrons, when the particles do not interact with each other, i.e. when there are very few electrons compared with the number of available states.

Diffusion Profile: Constant Surface Concentration

Diffusion

Constant surface concentration

Surface concentration of dopant is same (C_s)
; no change with time



Boundary conditions:

i) C(0,t) = Cs , ii) C(∞, t) = 0

$$C(x,t) = C_s erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$

Diffusion length

Total number of dopant atoms per unit area (dose):

$$Q(t) = \int_0^\infty C(x,t)dx$$

Area under of the diffusion profile

$$Q(t) = \frac{2}{\sqrt{\pi}} C_s\sqrt{Dt} \cong 1.13 C_s\sqrt{Dt}$$

$A=\frac{1}{2}Cs\ X\ 2\sqrt{Dt}=Cs\ \sqrt{Dt}$

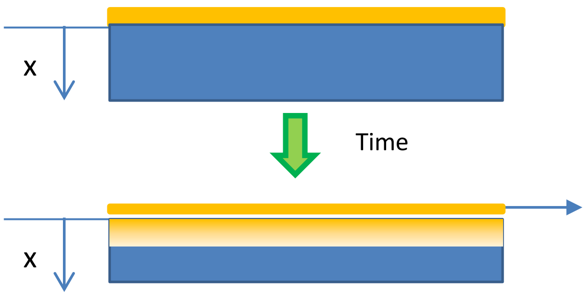
Correction constant

The gradient of diffusion profile (a related quantity):

$$\frac{\partial C}{\partial x}\Big|_{x,t} = \frac{C_s}{\sqrt{\pi Dt}} e^{-x^2/4Dt}$$

Diffusion Profile: Constant Total Dopant

Constant total dopant (Limit source diffusion)



A fixed amount of dopant
; Cs change with time

Cs is decreased
But, total amount is same

$$\int_0^\infty C(x,t) = Q\ (constant), \qquad C(\infty,t) = 0$$

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2}$$

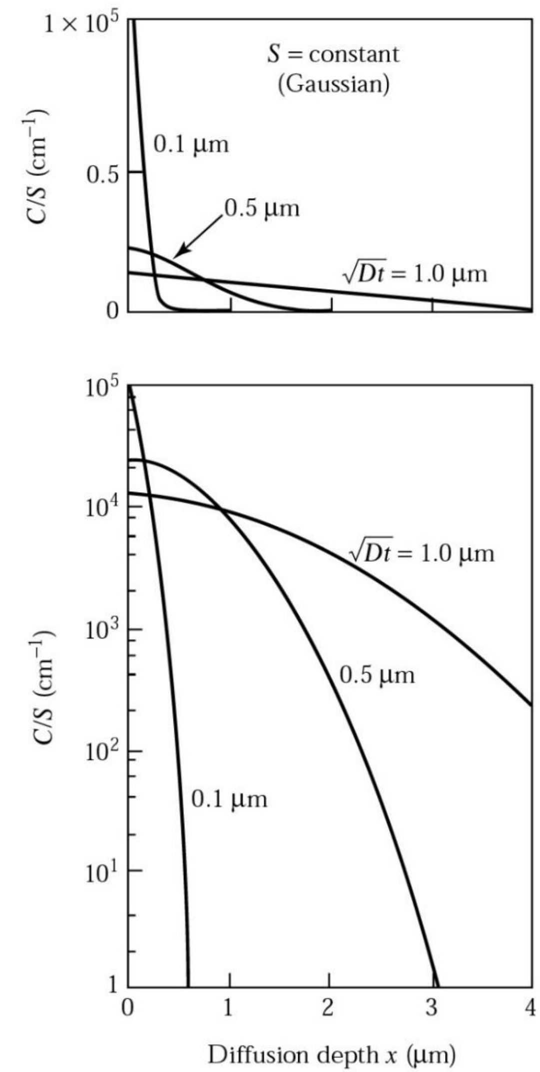
$$C(x,t) = \frac{Q}{\sqrt{\pi D t}}\exp\left(\frac{-x^2}{4Dt}\right)$$

$C.F)\ C(x,t) = C_s erfc\left(\frac{x}{2\sqrt{Dt}}\right)$

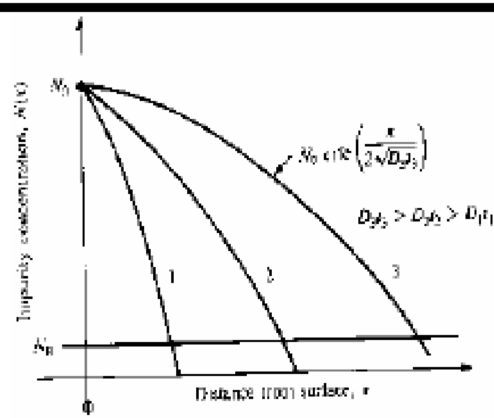
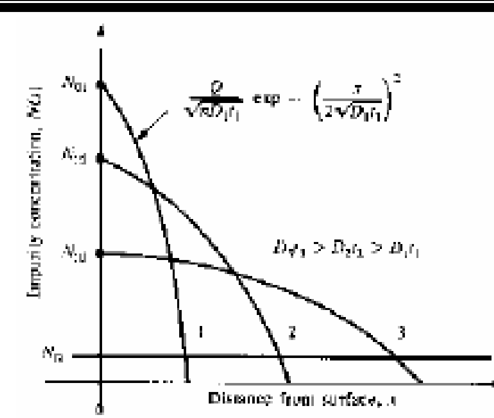
$$C(0,t) = \frac{Q}{\sqrt{\pi D t}}$$

Surface concentration decrease with time

$$\frac{\partial C}{\partial x}\Big|_{x,t} = -\frac{xQ}{2\sqrt{\pi}(Dt)^{\frac{3}{2}}} = -\frac{x}{2Dt}\,C(0,t)$$: The gradient of diffusion profile



Diffusion

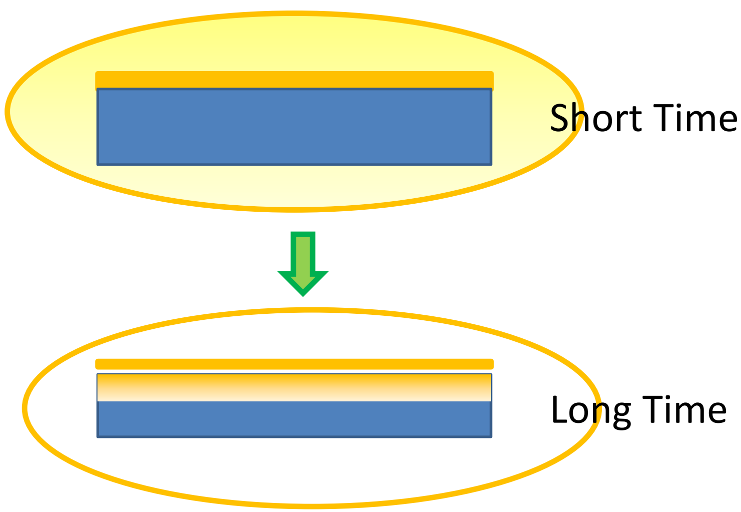
	Constant-source diffusion	Limited-source diffusion
Solution of equation (a)	$N(x,t) = N_0 erfc\left(\frac{x}{2\sqrt{Dt}}\right)$	$N(x,t) = \frac{Q_0}{\sqrt{\pi Dt}} \exp\left[-\left(\frac{x}{2\sqrt{Dt}}\right)^2\right]$
Impurity distribution	 "complementary error function"	 "Gaussian distribution"
Dose (Q) ≡Total # of Impurity atoms per unit area [atom/cm^2]	$Q = \int_0^\infty N(x,t)dx = 2N_0\sqrt{\frac{Dt}{\pi}}$	Q_0

Two-Step Diffusion

Diffusion

Two-step diffusion (general process)

1. Pre-depostion : Constant surface concentration (D_1t_1)
2. Drive-in (Redistribution) : Constant total dopant (D_2t_2)



If $D_1t_1 >> D_2t_2$: erfc distribution

$D_1t_1 << D_2t_2$: gaussian distribution

Successive diffusion

- We are interested in the final impurity distribution after all processing is complete.
- A wafer typically goes through many time-temperature cycles during pre-deposition, drive-in, oxide growth, CVD, etc.
- The effect of these steps is determined by calculating the total Dt for all high-temperature cycles affecting diffusion

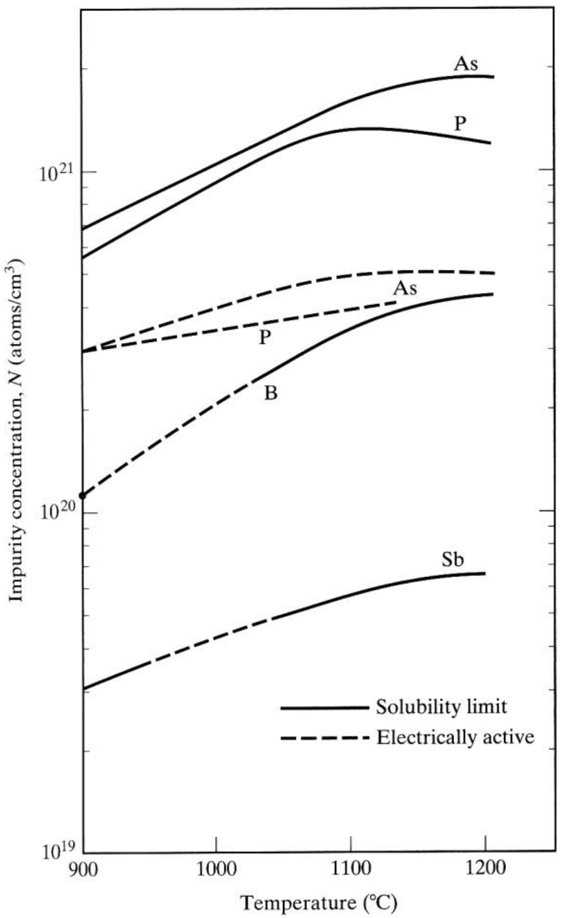
$$(Dt)_{total} = \sum_i D_i T_i$$

Solid Solubility Limits

Solid solubility limits

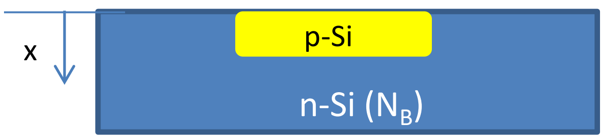
: At a given temperature, there is an upper **limit** to the amount of an impurity which can be **absorbed by silicon**

-At high concentrations, only a fraction of the impurities actually contribute holes or electrons for conduction. The dotted line shows the "electrically active" portion of the impurity concentration.



Evaluation of diffused layers

- Vertical diffusion and junction formation



i) Constant surface concentration (Erfc distribution)

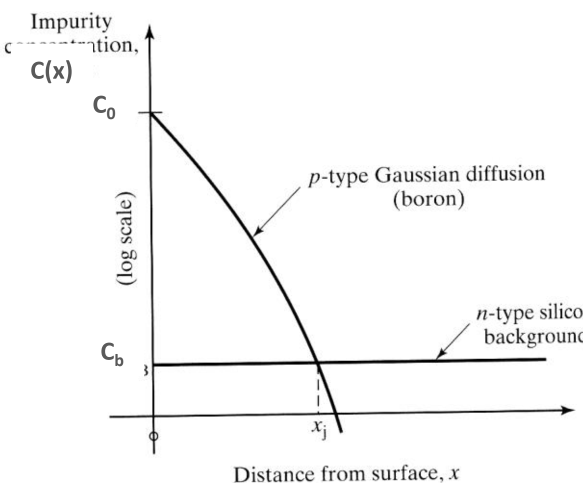
$$C(x,t) = C_s erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$

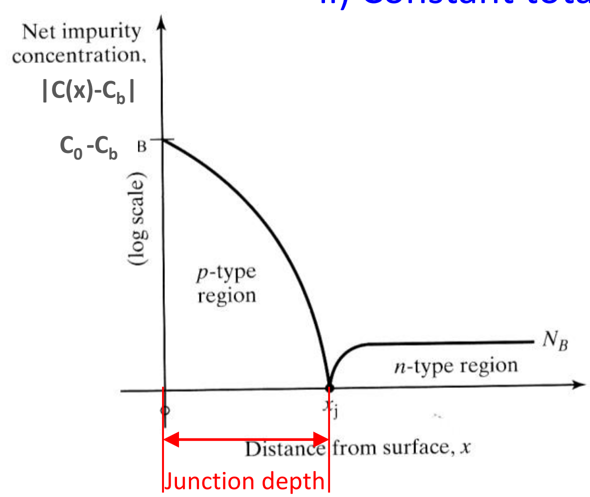
$$x_j = 2\sqrt{Dt} erfc^{-1}\left(\frac{C_b}{C_s}\right)$$

ii) Constant total dopant (Gaussian distribution)

$$C(x,t) = \frac{Q}{\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right)$$

$$x_j = 2\sqrt{Dt \cdot ln\left(\frac{C_0}{C_b}\right)}$$

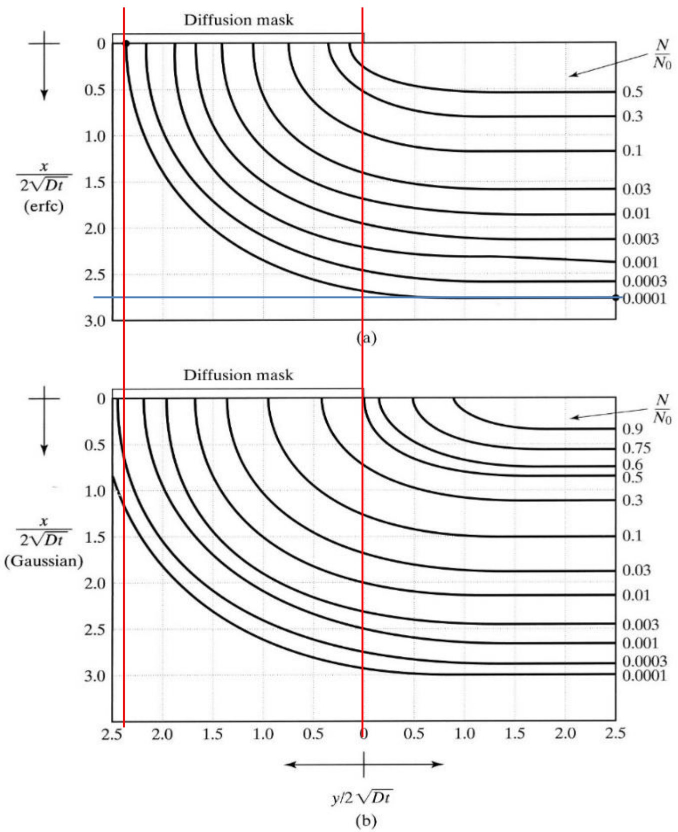


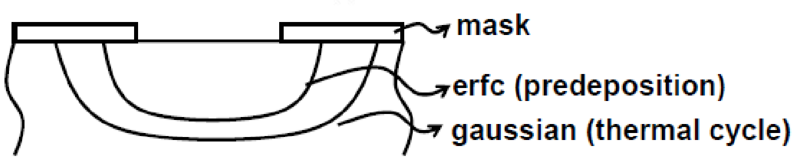


Direction: Lateral

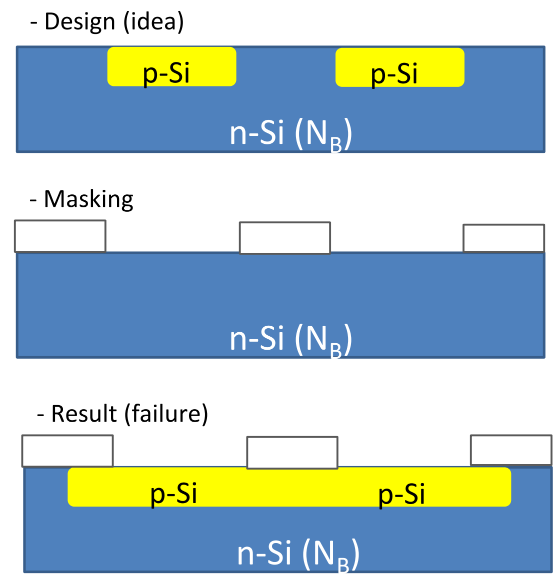
Diffusion

Lateral diffusion





- During diffusion, impurities not only diffuse vertically but also move laterally under the edge of any diffusion layer: important factor for design



Q) Constant surface diffusion, Junction depth is 2um, Cs=1x10^{20}/cm^3, C$_b$=1x10^{16}/cm^3.
the lateral diffusion underneath?

2.75 : 2.4 = 2 : X

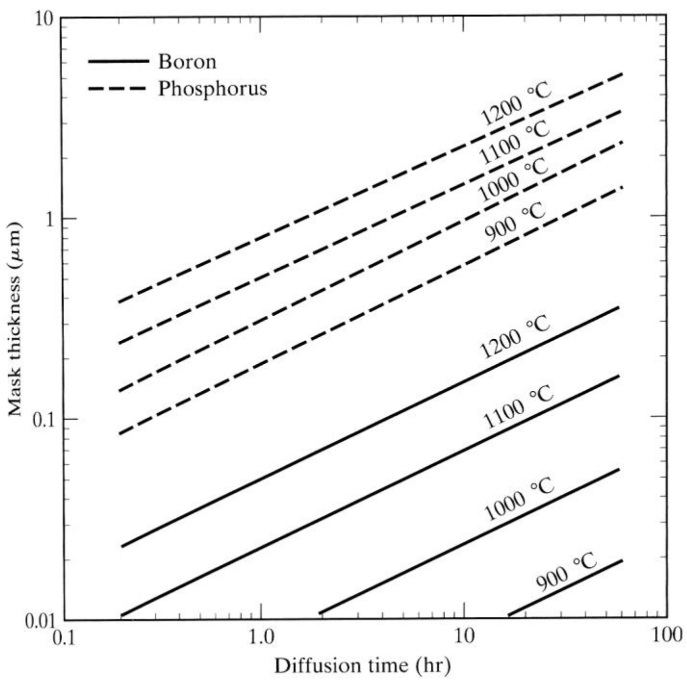
X= 1.74 um

Mask for Diffusion

Diffusion

- **Diffusion mask: SiO_2**

  - Diffusion rate to SiO_2 ≪ Diffusion rate to Si
    : Good mask for Sb, As, B, P



- More effective for B than P

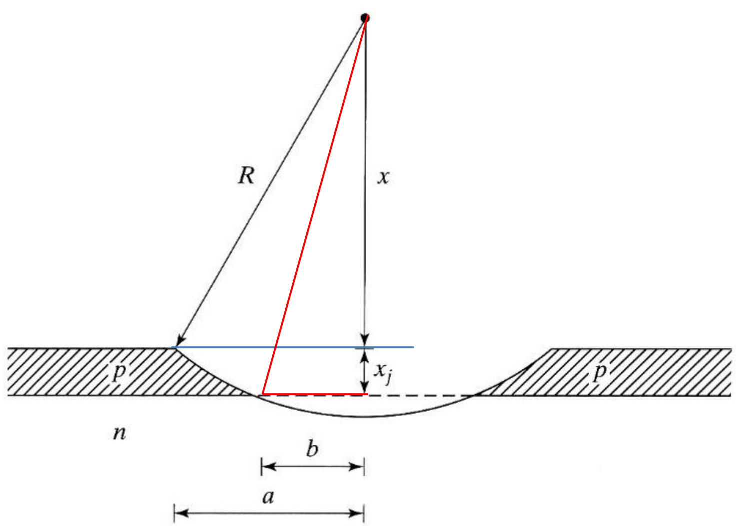
[note] SiO_2 is not good for Ga, Al as diffusion mask
→ Si_3N_4 is more effective

Evaluation of Diffusion Layers (1)

Junction depth measurement

- **Groove and stain method (Old method)**

  : Cylindrical groove is mechanically ground into the surface of the wafer



$$(x + x_j) - x = \sqrt{R^2 - b^2} - \sqrt{R^2 - a^2} = R\left(\sqrt{1 - \left(\frac{b}{R}\right)^2} - \sqrt{1 - \left(\frac{a}{R}\right)^2}\right)$$

$$\doteq R\left\{\left(1 - \frac{1}{2}\frac{b^2}{R^2}\right) - \left(1 - \frac{1}{2}\frac{a^2}{R^2}\right)\right\} \quad \begin{matrix} R >> a \\ R >> b \end{matrix}$$

$$x_j \doteq \frac{a^2 - b^2}{2R} = \frac{(a+b)(a-b)}{2R}$$

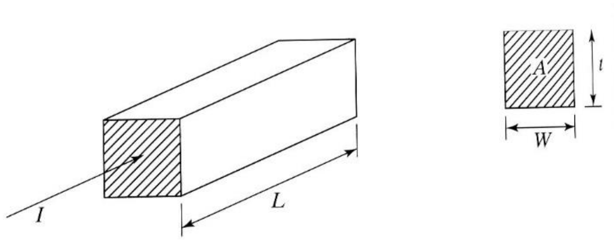
How to know the a, b value ?

i) 0.1% HF + 0.5% HNO3 with high intensity light

  : pn Junction color change

ii) Measure the a, b length using microscope

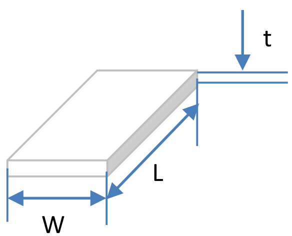
Sheet resistance



Resistance

$R = \rho L/A$

→ Resistivity (material's own property)



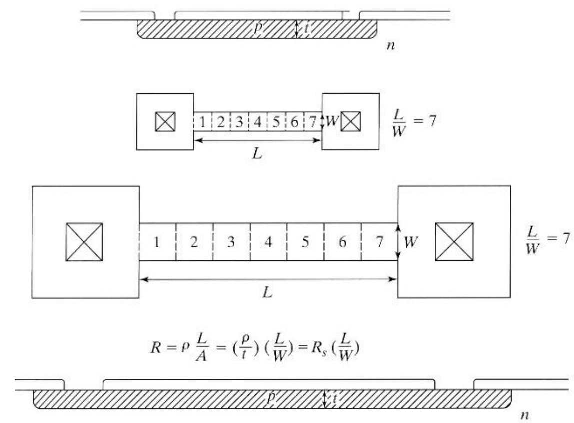
$R = \rho L/wt = (\rho/t)(L/w)$

→ Sheet resistance : R_s

Unit - R:Ω Rs :Ω/□
(□ , there is no meaning – to avoid confusion)

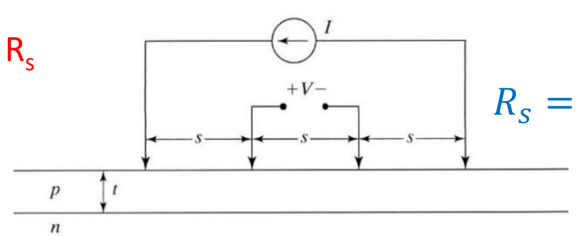
- Why we use sheet resistance for micro fabrication?

: Easy for design
; a circuit designer need specify only the length and width of the resistance to define its value.



Measuring sheet resistance

Measuring sheet resistance: four point probe
I : out side two probes, V; Inside two probes



$R_s = \rho/t = \frac{\pi}{ln2} \cdot \frac{V}{I}$ for t ≪ s

Evaluation of Diffusion Layers (3)

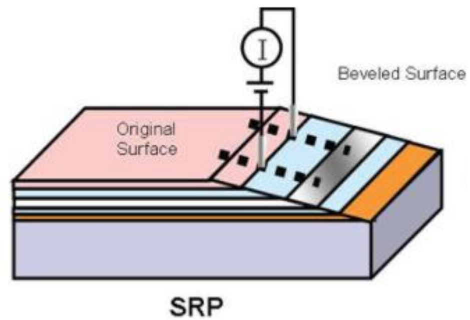
Diffusion

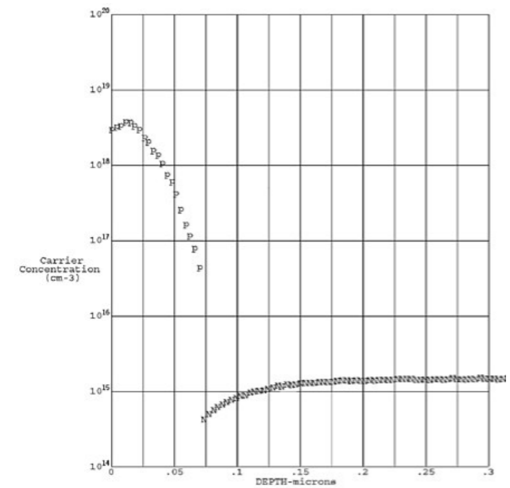
Capacitance-voltage technique

$$n = \frac{2}{q\varepsilon_s}\left[\frac{-1}{d\left(1/C'^2\right)/dV}\right]$$

q: the charge of an electron,
ε_s: the permittivity of the semiconductor,
C': capacitance per unit area of the sample
V: applied voltage

Spreading-resistance profiling (SRP)





Secondary Ion Mass Spectroscopy (SIMS)