

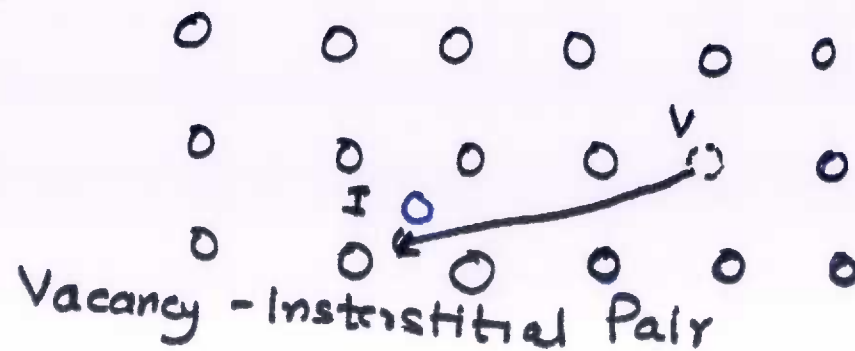
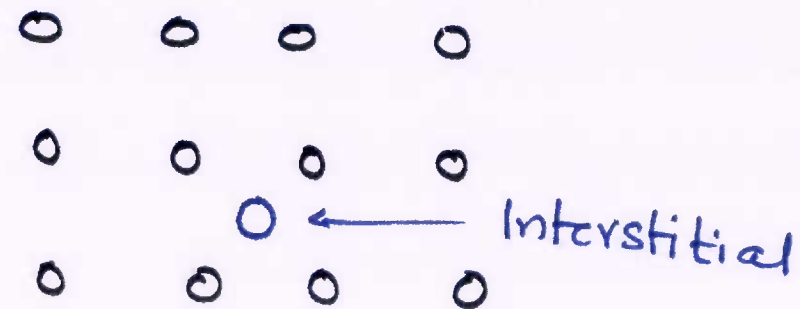
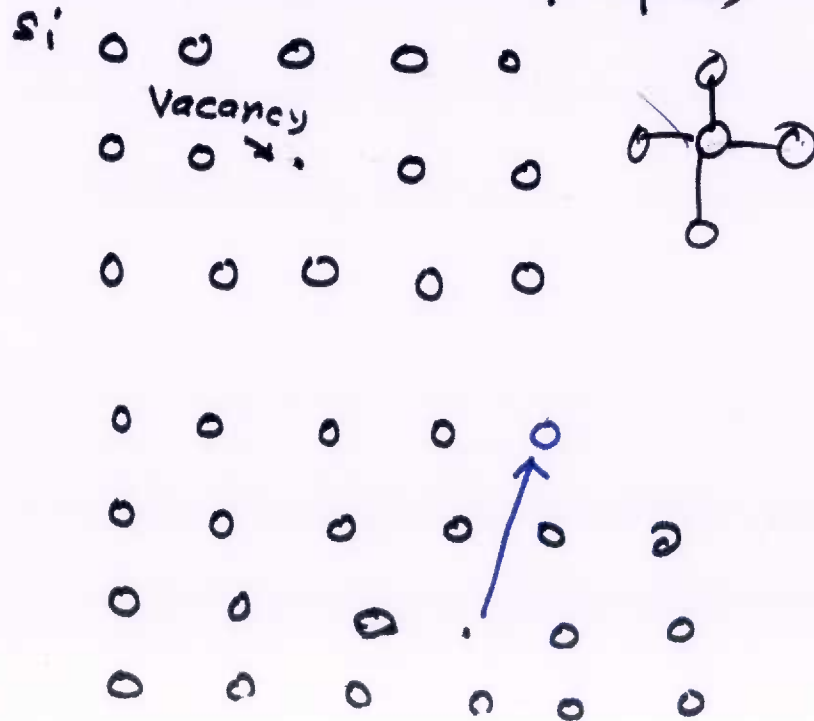


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Impurities can contribute to Resistivity, only if they occupy substitutional site in Silicon Crystal. Point Defects are very useful in impurity Incorporation. We recall these defects by figures shown below:

Vacancy (Schottky defect)





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Point Defects density is a function of Substrate Concentration (N atom/cc), activation energy and Temperature.

If n_s is no. of Defects/cc created in crystal of Concentration N atoms/cc

By Thermodynamic Principles, this defect density is due to availability of them in N atoms/cc at temp T .
Mathematically no of ways it can happen is

$$C_{n_s}^N = \frac{N!}{n_s! (N-n_s)!}$$

Further Entropy S of this system can be written as

$$S = k \ln [C_{n_s}^N]$$

$$\therefore T.S = kT \ln \left[\frac{N!}{n_s! (N-n_s)!} \right] \quad L = !$$

The Binding energy of atoms (Enthalpy) is given by

$$H = E_s \cdot n_s$$

where E_s is activation energy of the process

If Defects are to be Created, the Gibbs Free Energy G must first be evaluated and then optimised.

We have

$$G = n_s \cdot E_s - T.S \quad \left[(H - T.S) = G \right]$$

$$\text{or } G = n_s \cdot E_s - kT \left[\ln N! - \ln (N-n_s)! - \ln (n_s)! \right]$$

$$(G = H - TS)$$





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$$\begin{aligned}
 \alpha G &= n_s E_s - kT \left[N \ln(N) - N + (N-n_s) \ln(N-n_s) \right. \\
 &\quad \left. + (N-n_s) - n_s \ln n_s + n_s \right] \\
 &= n_s \cdot E_s - kT \left[N \ln N - (N-n_s) \ln(N-n_s) \right. \\
 &\quad \left. - n_s \ln n_s \right]
 \end{aligned}$$

We know
 $\ln x! = x \ln x - x$

By Thermodynamic Principles,
 maximum defects occurs when

when $\frac{dG}{dn_s} = 0$ (G minimum)

$$\begin{aligned}
 \therefore \frac{dG}{dn_s} = 0 &= E_s - kT \left[0 - \frac{(N-n_s)}{(N-n_s)} (-1) + \ln(N-n_s) \right. \\
 &\quad \left. - \frac{n_s}{n_s} - \ln n_s \right] \\
 0 &= E_s - kT \left[\ln(N-n_s) - \ln n_s \right]
 \end{aligned}$$



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$$\alpha \frac{E_s}{kT} = \ln\left(\frac{N-n_s}{n_s}\right)$$

$$\alpha e^{E_s/kT} = \frac{N-n_s}{n_s} = \frac{N}{n_s} - 1 \approx \frac{N}{n_s} \quad N \gg n_s$$

$$\therefore n_s = N e^{-E_s/kT}$$

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Hence if we know activation energy of Vacancy or Interstitial formation, then we can find their density at a temperature T .

Clearly n_s increases with increase of Temperature

Since Crystal Growths are at v. high temperature, there is very large probabilities of Creation of Vacancy & Interstitial.



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In General n_s for interstitial = N_{I0} is
different n_s for Vacancies = N_{V0}

In Equilibrium these conc. can be found
to fit to a model which gives

$$N_{I0} = N_{Si} \cdot e^{-E_{sI0}/kT}$$

$$\& N_{V0} = N_{Si} \cdot e^{-E_{sV0}/kT}$$

For Silicon these are

given by

$$N_{I0} = 10^{27} \exp[-3.8 \text{ eV} / kT]$$

$$N_{V0} = 9 \times 10^{23} \exp[-2.6 \text{ eV} / kT]$$



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By similar analysis we can find no of Frankel defects (Vacancy-Interstitial Pair) created at a given temperature

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If N is of number atoms in a crystal / Vol

N' = No of Available Interstitial Sites / Vol (out of N)

n_f = no of Frankel defect / Vol

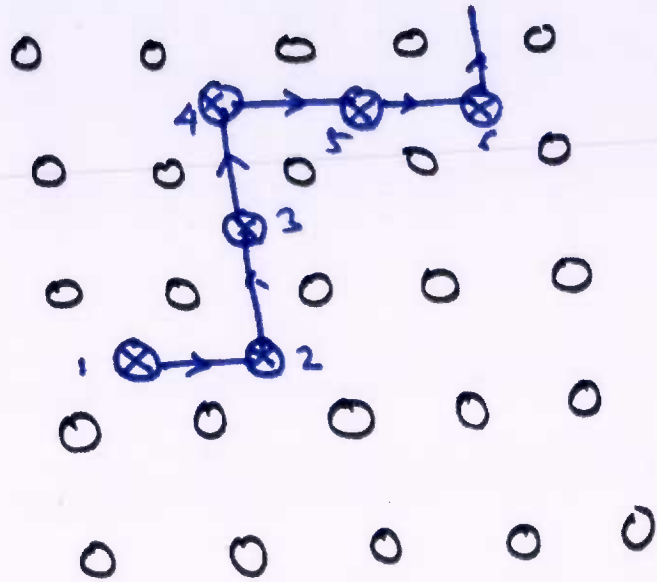
$k E_f$ = Activation energy, then

Entropy $S = k \ln (C_{n_f}^N C_{m_f}^{N'})$. Then doing similar analysis with Gibbs energy function we get

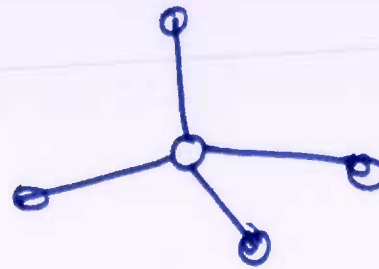
$$n_f = \sqrt{NN'} e^{-E_f/2kT} \quad E_f \text{ in Si} = 1.1 \text{ eV}$$

Nature of Diffusion

1. Interstitial Diffusion :



Primitive Lattice
of Silicon



Tetrahedral

In Silicon Lattice, we understand, there are 5 Voids (Interstitials) arranged Tetrahedrally. Some are occupied, but most are available sites for Impurities



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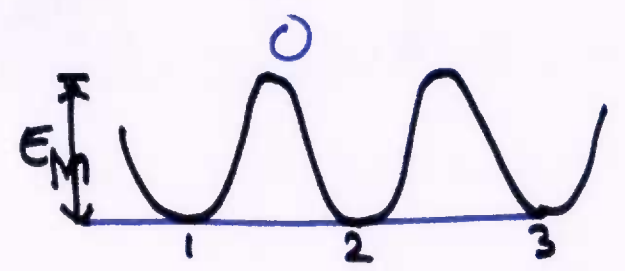
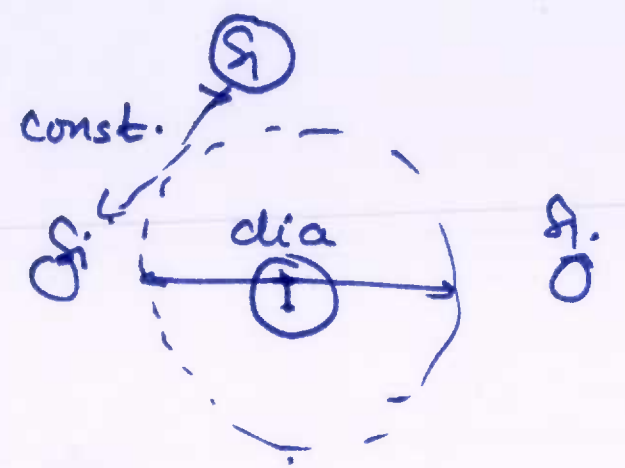
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L7. 5-8



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In Silicon diameter of Interstitial Void is 2.36 \AA
and Constrictions are of 2.10 \AA



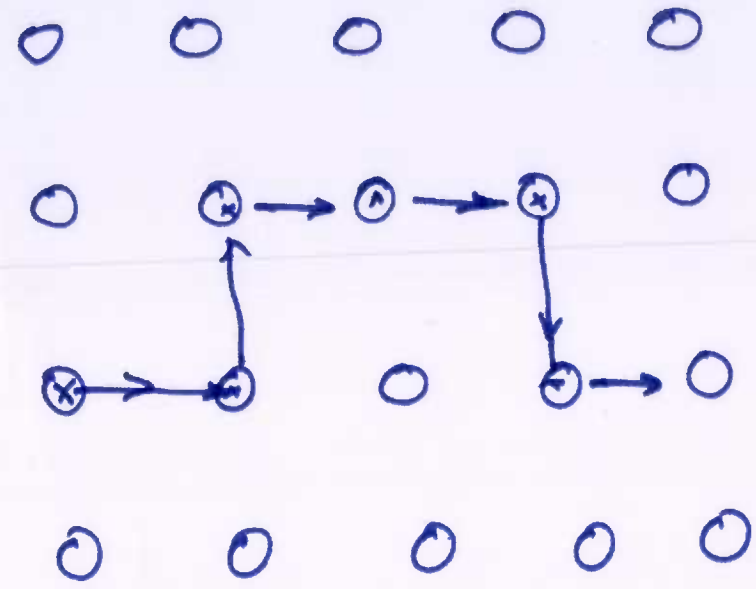
Since Lattice vibrates (even at Room temperature), it has frequency $\nu_0 = 10^{13}$ or 10^{14} /sec.

If Interstitial Impurity atom has to jump to another site, it has to overcome the energy barrier. At 700°C to 1200°C temperature, thermal vibrations occur with frequency ν [$f(T)$] (Jump f)

Then
$$\nu = 4\nu_0 e^{-E_m/kT}$$

where E_m is Barrier energy. 4 appears due to Degeneracy
Typically Model suggests that $E_m = 1\text{eV}$, & Jump Rate - 1/minute

Substitutional Diffusion



Diffusion is from one Substitutional site to another.

Essentially this is Vacancy Related process.

As no. of Vacancies are fewer than ~~Such~~ Interstitial sites, the jump rate of this Diffusion Process is smaller.

We can write

$$v \propto e^{-E_n/kT} \quad \text{where } E_n \text{ is Barrier energy}$$

However Occurance of vacancies are proportional to $e^{-E_s/kT}$ (Binding Energy).

$$\therefore v = 4v_0 e^{-(E_n + E_s)/kT}$$

Si-Si Bond 'BE' is larger than Si-Impurity BE.

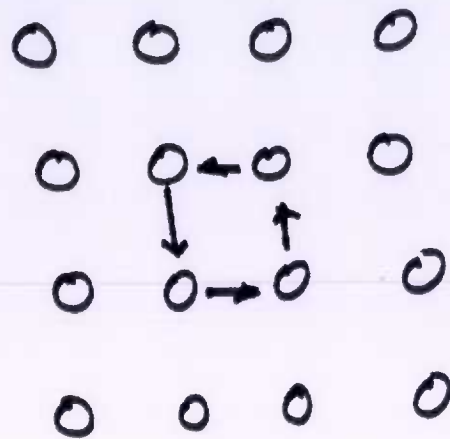
Hence Self Diffusion of Silicon is much smaller than Impurity Diffusion



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(iii) Interchange Diffusion



Very Small probability of such Diffusion

(iv) Combinational Diffusion

Both substitutional & interstitial Diffusion of Impurity. This process has large Probability of Occurrence



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If N_s and N_i are concentration of available substitutional and interstitial sites at Temp. T , then effective Jump frequency ν_{eff} can be :

$$\nu_{eff} = \frac{\nu_s N_s}{N_s + N_i} + \frac{\nu_i N_i}{N_s + N_i}$$

Conc of Both defects relative to each other ν_{eff} .

Important :- However it is important to note that Natural random jump events may not be v. large, However Concentration Gradient of Impurities will dominate the Diffusion Process



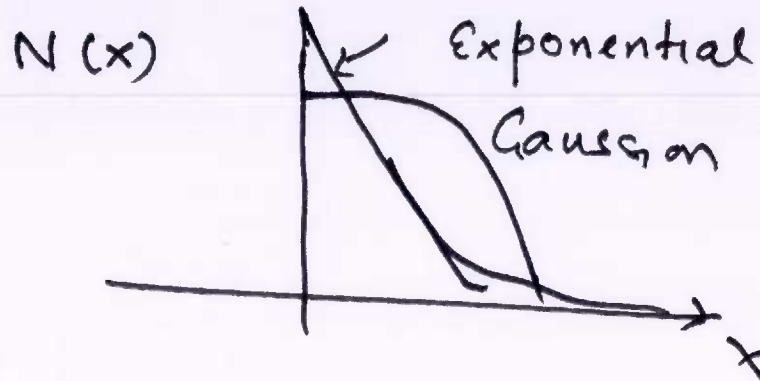
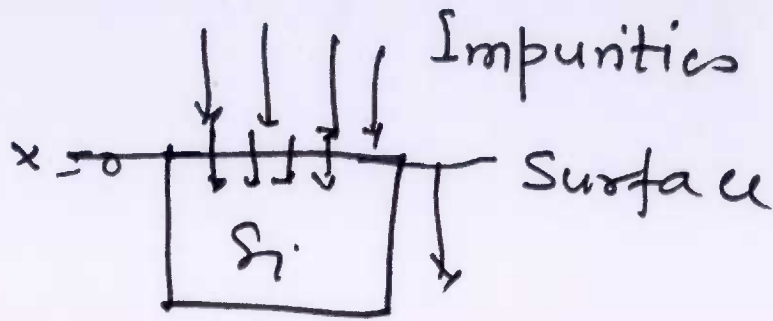
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$$\underline{\underline{N(x)}} = ?$$

$n(x)$ $p(x)$

Silicon Conc $\rightarrow 5 \times 10^{22} / \text{cc}$

$$\gamma = \gamma_0 (1 \pm \epsilon)$$

$\epsilon =$ Misfit Factor



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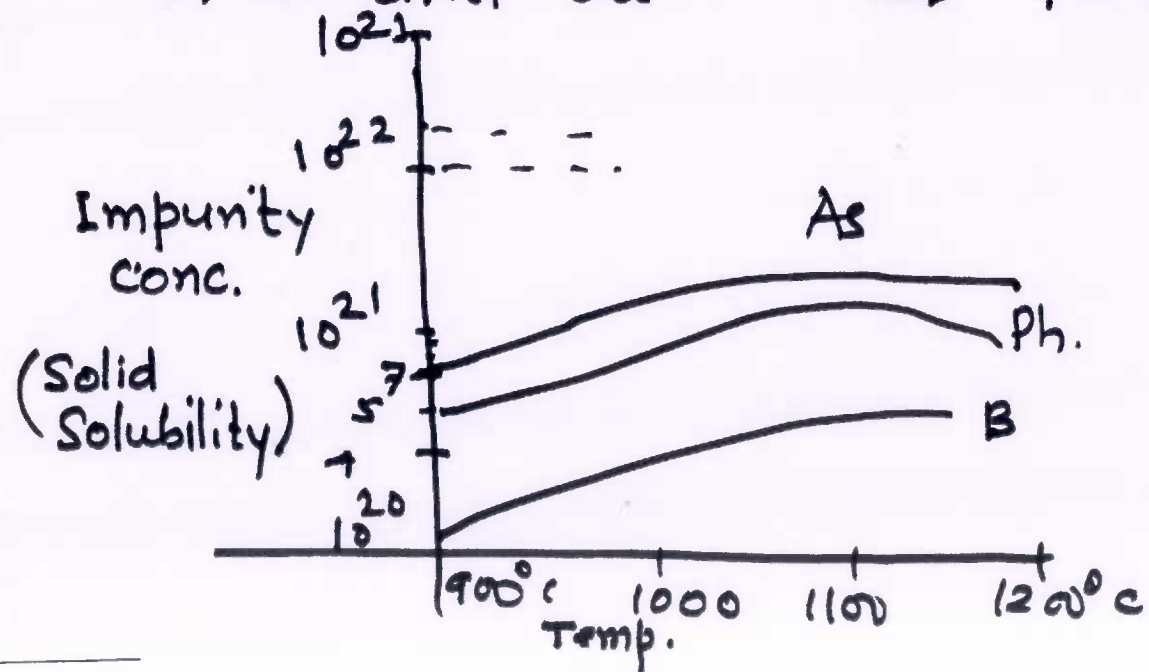
Basics of Impurity Transport in Silicon.

Solid state Diffusion is characterised by

Types of Impurities, Temperature and Time of Diffusion.

As, Phosphorous, Sb, → N-Type Impurities

B, Al and Ga → P-type Impurities



Maximum Impurity Conc which can be incorporate in another lattice without disturbing Lattice Structure, at a Given Temperature is called Solid Solubility

Modeling Point Defects in Silicon

Impurity in Silicon lattice

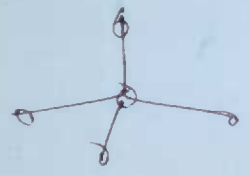
Leads to Strain

Tetrahedral Radii

Si	$r_0 = 1.18 \text{ \AA}$	
P	1.10	0.068
As	1.18	0
B	0.88	0.254
Al	1.026	0.068
Ge	1.26	0.068
In	1.44	0.22
Au	1.5	0.272
Aj	1.52	0.29

recb Imp.

$$r = r_0(1 \pm \epsilon)$$



- Point defects (V and I) will turn out to play fundamental roles in many process technologies.
- The total free energy of the crystal is minimized when finite concentrations of these defects exist.

$$C_{I^0}^* , C_{V^0}^* = N_S \exp\left(\frac{S^f}{k}\right) \exp\left(\frac{-H^f}{kT}\right) \quad (17)$$

- In general $C_{I^0}^* \neq C_{V^0}^*$ and both are strong functions of temperature.
- Kinetics may determine the concentration in a wafer rather than thermodynamics.
- In equilibrium, values for these concentrations are given by:

$$C_{I^0}^* \equiv 1 \times 10^{27} \exp\left(\frac{-3.8 \text{ eV}}{kT}\right) \quad (18)$$

$$C_{V^0}^* \equiv 9 \times 10^{23} \exp\left(\frac{-2.6 \text{ eV}}{kT}\right) \quad (19)$$

- These equations give $C_{I^0}^*$ & $C_{V^0}^* \approx 0$ at room T and $10^{12} - 10^{14} \text{ cm}^{-3}$ at $1000 \text{ }^\circ\text{C}$ - too small to measure.

The transport of Impurities in Silicon is governed by two Laws

(i) Fick's First Law

(ii) Fick's Second Law.



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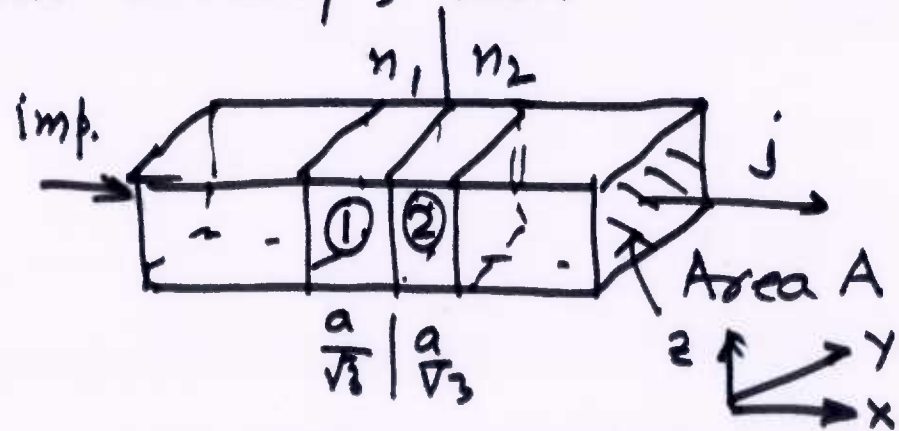
(i) Fick's First Law

If j is the ~~net~~ ^{net} Flux Density, then

$$j = \frac{1}{A} \cdot \frac{dn}{dt}$$

Net rate of species crossing
① to ② planes is $\frac{dn}{dt}$

$$= - \frac{VAa}{2\sqrt{3}} \frac{a}{\sqrt{3}} \frac{dN}{dx}$$



where $\frac{dN}{dx} = \frac{N_2 - N_1}{a/\sqrt{3}}$

where N is net concentration across the Plane ① to Plane ②

$$\text{If we define } D = \frac{v a^2}{6}$$

$$\therefore \frac{1}{A} \frac{dn}{dt} = - D \frac{dN}{dx} = - D \frac{\partial N}{\partial x}$$

$$D_r \quad j = - D \frac{\partial N}{\partial x}$$

Statement of Fick's 1st Law.

$$\text{The Diffusion Coeff. } D = \frac{4 v_0 a^2}{6} \exp \left[- (E_N + E_s) / kT \right]$$

$$\text{or } D = D_0 \exp \left[- (E_N + E_s) / kT \right]$$



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(ii) Fick's IInd Law

This is essentially a Statement of Continuity Equation.

Using Divergence theorem, the flux density j can be written

$$j = -D \frac{\partial N}{\partial x} \quad \text{and} \quad \frac{dj}{dx} = - \frac{dN}{dt}$$

$$\therefore \boxed{\frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2}}$$

This is called Diffusion Equation.



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This equation is derived for case where one assumes Diffusion Coeff $D = \text{constant}$.

In case D is $f(N)$ or $f[N(x)]$

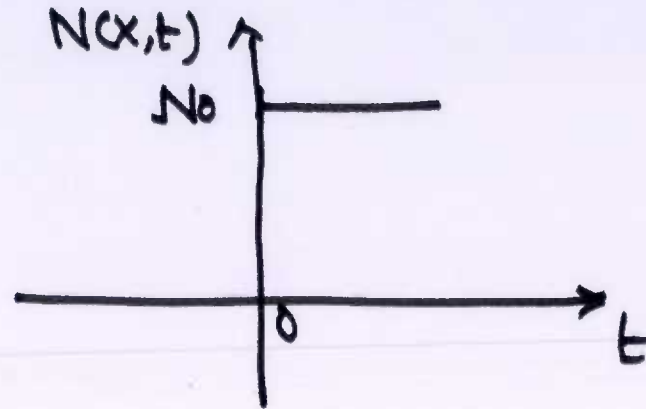
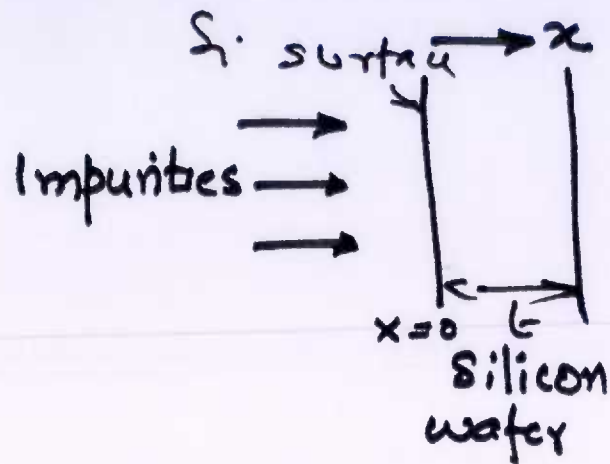
Then $D = f(x)$

$$\text{As } J = -D(x) \frac{\partial N}{\partial x}$$

$$\text{Then } \frac{dj}{dx} = -D \frac{\partial^2 N}{\partial x^2} - \frac{\partial D}{\partial x} \cdot \frac{\partial N}{\partial x}$$

$$\text{Then } \boxed{\frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2} + \frac{\partial D}{\partial x} \cdot \frac{\partial N}{\partial x}}$$

Diffusion Profiles :



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From Fick's Second Law

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

This is called Diffusion Eq.

Taking Laplace Transform

$$s \{ N(x, s) \} - N(x, t=0) = D \frac{\partial^2 N(x, s)}{\partial x^2} \quad - (1)$$

$$\text{or } \frac{d^2 N(x,s)}{dx^2} = \frac{s}{D} N(x,s) - \frac{N(x,t=0)}{D} \quad \text{--- (ii)}$$



Let us assume impurity source provides impurities at the surface of the wafer ($x=0$) at $t=0$. Which means $N(x,t=0) \leq 0$ --- (iii)

However at $t=0^+$, source of impurities are at the surface. Thus impurity source is like Unit Step function in time as shown.

Our next assumption is that impurity source keeps constant impurity concentration at $x=0$ for all time to come. This value is defined as N_0

$$\sim N(x, t_0^+) = N_0 = \text{constant} \quad - (iv)$$

Solution of Differential Equation (ii) is

$$N(x, s) = A(s) \exp \left\{ \left(\frac{s}{D} \right)^{1/2} x \right\} + B(s) \left\{ \exp \left[\left(-\frac{s}{D} \right)^{1/2} x \right] \right\}$$

Where $A(s)$ & $B(s)$ are unknown Pre-exponents. $- (v)$

Boundary Conditions :

At $x = \infty$ first term $\rightarrow \infty$. This is against

Diffusion Principle (Gradient based motion)

$$\therefore A(s) = 0 \quad - (vi)$$

$$\therefore N(x, s) = B(s) \exp \left[\left(-\frac{s}{D} \right)^{1/2} x \right] \quad - (vii)$$



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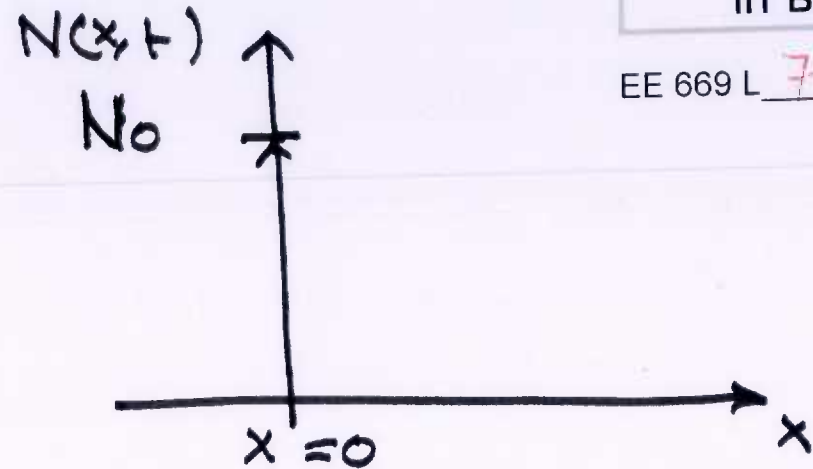
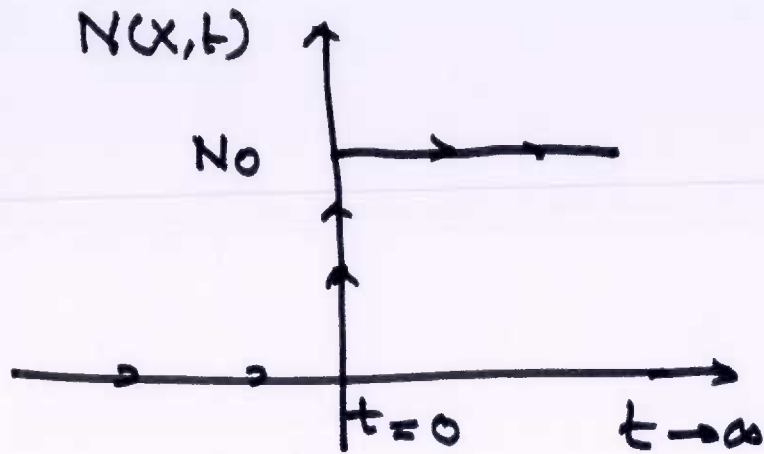
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We have two Figures to show initial & BCs.



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The second Boundary Condⁿ is that at the Silicon surface ($x=0$) constant source of impurities are present = N_0 , i.e.

$$N(x=0, t) = N_0 u(t) \quad - \quad (viii)$$

This condition is also called Infinite Source condition. Taking Laplace transform of IInd BC

$$\text{We have } N(x=0, s) = \frac{N_0}{s} \quad \text{--- (ix)}$$

Substituting this into eq. (vii), we have

$$N(x=0, s) = \frac{N_0}{s} = B(s) \exp\{0\} = B(s)$$

Hence final solution of the Diffusion Equation for Infinite Source case is

$$N(x, s) = \frac{N_0}{s} \exp\left\{\left(-\frac{s}{D}\right)^{1/2} x\right\} \quad \text{--- (xi)}$$



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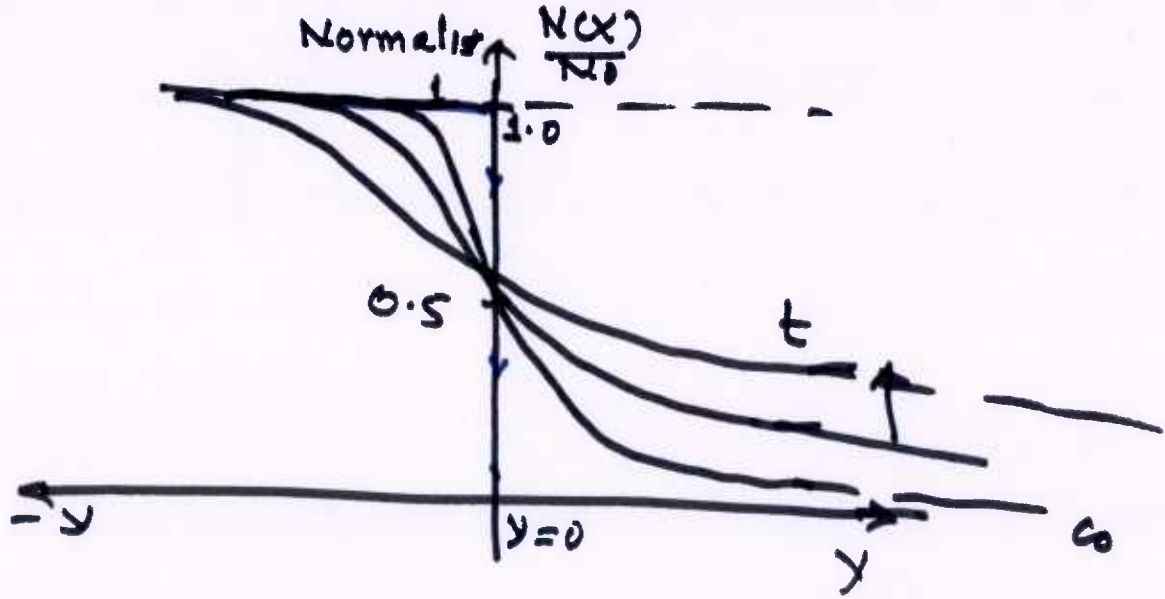
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Taking Inverse Laplace Transform, we get

$$N(x,t) = N_0 \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad \text{---(xii)}$$

$$\text{or } N(x,t) = N_0 \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) \quad \text{--- (xiii)}$$

The plot of this $N(x,t)$ is :



We define

$$y = \frac{x}{2\sqrt{Dt}} \text{ as } x=0 : y=0$$

$$x=\infty : y=\infty$$

$$\sqrt{Dt} = \text{cm}$$

$$\sqrt{\frac{\text{cm}^2}{\text{sec}} \times \text{sec}}$$

Error function Algebra

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx$$

$$\operatorname{erf}(x=0) = 0$$

$$\operatorname{erf}(x=\infty) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-x^2} dx$$

$$= 1 = \left(\frac{2}{\sqrt{\pi}} \cdot \frac{\sqrt{\pi}}{2} \right)$$

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$$

$$\text{As } \int_0^{\infty} e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$$

$$\frac{d}{dx} [\operatorname{erf}(x)] = \frac{2}{\sqrt{\pi}} \exp(-x^2)$$

$$\frac{d^2}{dx^2} [\operatorname{erf}(x)] = -\frac{4}{\sqrt{\pi}} x e^{-x^2}$$

$$\int_0^{\infty} e^{-y^2} dy = y - \frac{y^3}{(3 \times 1)!} + \frac{y^5}{5 \times 2!} - \frac{y^7}{7 \times 3!} - \dots$$



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