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

Vacancy (Schottky defect)

Vacancy - Interstitial Pair
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

\[
S = k \ln \left[ C_{n_s}^N \right]
\]
\[ T.S = kT \ln \left[ \frac{N!}{\eta_s!(N-\eta_s)!} \right] \]

The Binding energy of atoms (Enthalpy) is given by

\[ H = E_s \cdot \eta_s \]

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

\[ G = \eta_s \cdot E_s - T \cdot S \quad (H - T \cdot S) = G \]

or \( G = \eta_s \cdot E_s - kT \left[ \ln N! - \ln (N-\eta_s)! - \ln (\eta_s)! \right] \)

\( (G = H - T \cdot S) \)
\[ \alpha \ G = \eta_s E_s - kT \left[ N_+ \ln(N_+) - N_- \ln(N-\eta_s) + (N-\eta_s) \ln N - \eta_s \ln \eta_s + \eta_s \right] \]

\[ = \eta_s E_s - kT \left[ N \ln N - (N - \eta_s) \ln (N - \eta_s) - \eta_s \ln \eta_s \right] \]

By Thermodynamic Principles, maximum defect occurs when \( \frac{dG}{d\eta_s} = 0 \) (\( G \) minimum)

\[ \frac{dG}{d\eta_s} = 0 = E_s - kT \left[ 0 - \frac{(N - \eta_s)}{(N - \eta_s)} (-1) + \ln (n-\eta_s) \right. \]

\[ - \left. \frac{\eta_s}{\eta_s} - \ln \eta_s \right] \]

\[ 0 = E_s - kT \left[ \ln (n-\eta_s) - \ln \eta_s \right] \]
\[ \frac{E_s}{kT} = \ln \left( \frac{N-n_s}{n_s} \right) \]

\[ e^{E_s/kT} = \frac{N-n_s}{n_s} = \frac{N}{n_s} - 1 \approx \frac{N}{n_s} \quad n_s \ll N \]

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

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 very high temperature, there is very large probabilities of Creation of Vacancy & Interstitial.
In General $N_s$ for interstitial = $N_{i0}$ is different $N_s$ for Vacancies = $N_{v0}$.

In equilibrium these concentrations can be found to fit to a model which gives

$$N_{i0} = N_{Si} e^{-E_{Si0}/kT}$$

and

$$N_{v0} = N_{Si} e^{-E_{v0}/kT}.$$  

For Silicon these are given by

$$N_{i0} = 10^{27} \exp \left[-\frac{3.8 \text{ eV}}{kT}\right]$$

$$N_{v0} = 9 \times 10^{23} \exp \left[-\frac{2.6 \text{ eV}}{kT}\right].$$
By similar analysis we can find no of Frankel defects (Valency-Interstitial Pair) created at a given temperature.

If $N$ is no of atoms in a crystal /vol

$$N' = \text{No of Available Interstitial Sites} /\text{vol (out of N)}$$

$\eta_f = \text{no of Frankel defects /vol}$

$k E_f = Activation\ energy$, then

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

$$\eta_f = \sqrt{NN'} \ e^{-E_f/2kT}$$

$E_f$ in Si = 1.1 ev
Nature of Diffusion

1. Interstitial Diffusion:

![Diagram of 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.
In Silicon diameter of Interstitial Void is 2.36 Å and Constrictions are of 2.10 Å

Since Lattice vibrates (even at Room Temperature), it has frequency \( v_0 = 10^{13} \text{ or } 10^{14} \text{ sec}^{-1} \). Impurity

If Interstitial 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 \( v \ [f(T)] \) (Jump)

Then \( v = 4v_0 \exp \left(-\frac{E_m}{kT}\right) \)

where \( E_m \) is Binding energy. \( 4 \) appears due to Degeneracy

Typically model suggests that \( E_m = 1 eV \), and 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 Sub Interstitial Sites, the jump rate of this Diffusion Process is Smaller.
We can write
\[ \nu \propto e^{-E_b/kT} \]
where \( E_b \) is the barrier energy.

However, occurrence of vacancies are proportional to \( e^{-E_b/kT} \) (binding energy).

\[ \therefore \nu = \nu_0 e^{-(E_b+E_s)/kT} \]

Si-Si bond `BE' is larger than Si-impurity BE. Hence, self diffusion of silicon is much smaller than impurity diffusion.
(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.
If $N_s$ and $N_I$ are concentration of available substitutional and interstitial sites at Temp. $T$, then effective jump frequency $V_{eff}$ can be:

$$V_{eff} = \frac{V_s N_s}{N_s + N_I} + \frac{V_I N_I}{N_s + N_I}$$

Conc of both defects relative to each other

Important: - However it is important to note that natural random jump events may not be very large. However, concentration gradient of impurities will dominate the diffusion process.
\[ N(x) = ? \]
\[ n(x) = p(x) \]

Silicon Conc. \( \rightarrow 5 \times 10^{22} \text{/cc} \)

\[ \gamma = \gamma_0 (1 \pm \epsilon) \quad \epsilon = \text{Misfit Factor} \]
Basics of Impurity Transport in Silicon.
Solid State Diffusion is characterised by Types of Impurities, Temperature and Time of Diffusion.

As, Phosphorous, Sb, \(\rightarrow\) N-Type Impurities
B, Al and Ga \(\rightarrow\) P-Type Impurities

Maximum Impurity Concentration which can be incorporated in another lattice without disturbing lattice structure, at a given temperature is called Solid Solubility.
Modeling Point Defects in Silicon

- 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.

\[
C_{I^0}^* \cdot C_{V^0}^* = N_S \exp\left(\frac{S_f}{k}\right) \exp\left(-\frac{H_f}{kT}\right)
\]  

(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:

\[
C_{I^0}^* = 1 \times 10^{27} \exp\left(-\frac{3.8\text{eV}}{kT}\right)
\]

(18)

\[
C_{V^0}^* = 9 \times 10^{23} \exp\left(-\frac{2.6\text{eV}}{kT}\right)
\]

(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 °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.

(i) Fick's First Law

If \( j \) is the net flux density, then

\[ j = \frac{1}{A} \cdot \frac{dn}{dt} \]

Net rate of species crossing \( 1 \) to \( 2 \) planes is

\[ \frac{dN}{dx} = \frac{N_2 - N_1}{a/\sqrt{3}} \]
where $N$ is net concentration across the Plane 1 to Plane 2

If we define $D = \frac{2a^2}{5}$

\[ \frac{1}{A} \frac{dN}{dt} = -D \frac{dN}{dx} = -D \frac{\partial N}{\partial x} \]

\[ I = -D \frac{\partial N}{\partial x} \quad \text{Statement of Fick's 1st Law.} \]

The Diffusion Coeff. $D = \frac{42 \nu_0 a^2}{5} \exp \left[ \frac{-(E_N + E_S)}{kT} \right]$ 

$\sigma = D_0 \exp \left[ \frac{-(E_N + E_S)}{kT} \right]$
(ii) Fick's 2nd Law

This is essentially a statement of Continuity Equation.

Using Divergence theorem, the flux density $j$ can be written

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

\[ \therefore \frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2} \]

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

In case $D$ is $f(N) \propto f(N(x))$

Then $D = f(x)$

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

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

Then $\frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2} + \frac{\partial D}{\partial x} \cdot \frac{\partial N}{\partial x}$
Diffusion Profiles:

From Fick's Second Law

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

Taking Laplace Transform

\[ S \mathcal{L} N(x,s) = N(x,t=0) = D \frac{\partial^2 N(x,s)}{\partial x^2} \]
or \[ \frac{d^2 N(x,s)}{dx^2} = \frac{S}{D} N(x,s) - \frac{N(x, t=0)}{D} \] 

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 No
\[ N(x, t_0^+) = N_0 = \text{constant} \quad (\text{IV}) \]

Solution of Differential Equation (II) is

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

Where \( A(s) \) & \( B(s) \) are unknown pre-exponents. \( (V) \)

Boundary Conditions:

At \( \infty \), first term \( \rightarrow \infty \). This is against Diffusion Principle (Gradient based motion)

\[ A(s) = 0 \quad (VI) \]

\[ \therefore N(x, t) = B(s) \exp \left[ \left( \frac{-s}{D} \right)^{\frac{1}{2}} x \right] \quad (VII) \]
We have two figures to show Ionized & BCs.

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

\[ N(x=0, t) = N_0 \mu(t) \]  

(viii)
This condition is also called Infinite Source condition. Taking Laplace transform of II\textsuperscript{nd} BC, we have

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

Substituting this into eq. (vii), we have

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

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

$$N(x, s) = \frac{N_0}{s} \exp \left\{ \left( -\frac{s}{D} \right)^{\frac{1}{2}} x^2 \right\}$$
Taking Inverse Laplace Transform, we get

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

\[ N(x,t) = N_0 \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \quad (xiii) \]

The Plot of this \( N(x,t) \) is:

We define

\[ y = \frac{x}{2\sqrt{Dt}} \quad a_0 \quad x = 0 \quad y = 0 \]

\[ x = a_0 \quad y = a \]

\[ \sqrt{Dt} = \frac{cm}{\sqrt{2\pi} \sigma} \]
Error Function Algebra

\[ \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} \, dx \]

\[ \text{erf}(x = 0) = 0 \quad \text{erf}(x = \infty) = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-x^2} \, dx = 1 = \left( \frac{2}{\sqrt{\pi}} \cdot \frac{\sqrt{\pi}}{2} \right) \]

As \[ \int_0^\infty e^{-x^2} \, dx = \frac{\sqrt{\pi}}{2} \]

\[ \text{erfc}(x) = 1 - \text{erf}(x) \]

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

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

\[ \int_0^x e^{-y^2} \, dy = y - \frac{y^3}{(3 \times 1)!} + \frac{y^5}{(5 \times 2)!} - \frac{y^7}{(7 \times 3)!} \ldots \]