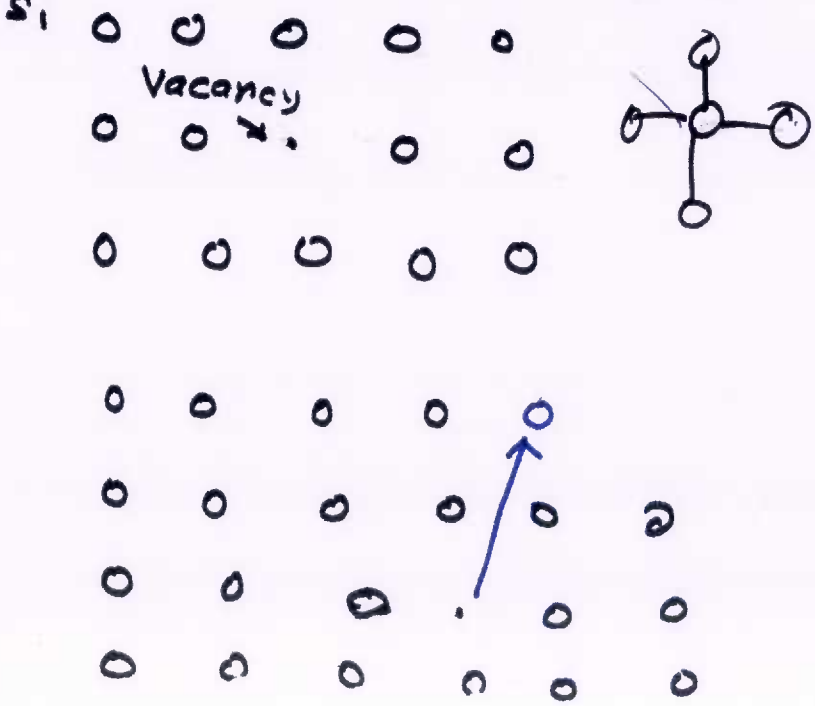
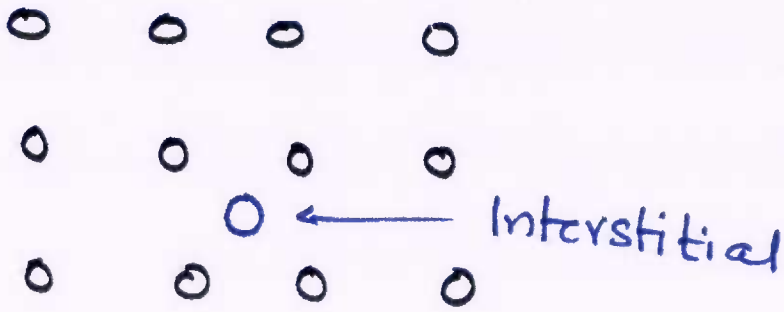
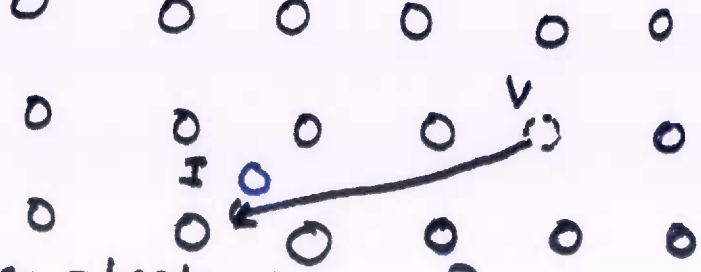
Impurities can contribute to Resistivity, only if the occupy substitutional site is Silicon Crystal. Point Defects are very useful in impurity Incorporation. We recall these defects by figures shown below:

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

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

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

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

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

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

$(G = H - TS)$

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

$$= n_s \cdot E_s - kT\left[N\ln N - (N-n_s)\ln(N-n_s) - n_s \ln n_s \right]$$

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

By Thermodynamic Principles, maximum defects occurs when $\frac{dG}{dn_s} = 0$ (G minimum)

$$\therefore \frac{dG}{dn_s} = 0 = E_s - kT\left[0 - \frac{(N-n_s)}{(N-n_s)}(-1) + \ln(n-n_s) - \frac{n_s}{n_s} - \ln n_s \right]$$

$$0 = E_s - kT\left[\ln(n-n_s) - \ln n_s \right]$$

$$\propto \frac{E_S}{kT} = \ln\left(\frac{N-n_s}{n_s}\right)$$

$$\propto e^{E_s/kT} = \frac{N-n_s}{n_s} = \frac{N}{n_s} - 1 \cong \frac{N}{n_s} \qquad N \gg n_s$$

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

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 v. 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 conc.. can be found to fit to a model which gives

$$N_{I0} = N_{Si}\, e^{-E_{SI_0}/kT}$$

& $N_{V0} = N_{Si}\, e^{-E_{SV0}/kT}$. For Silicon these are given by

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

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

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

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 defects/vol

& E_f = Activation energy, then

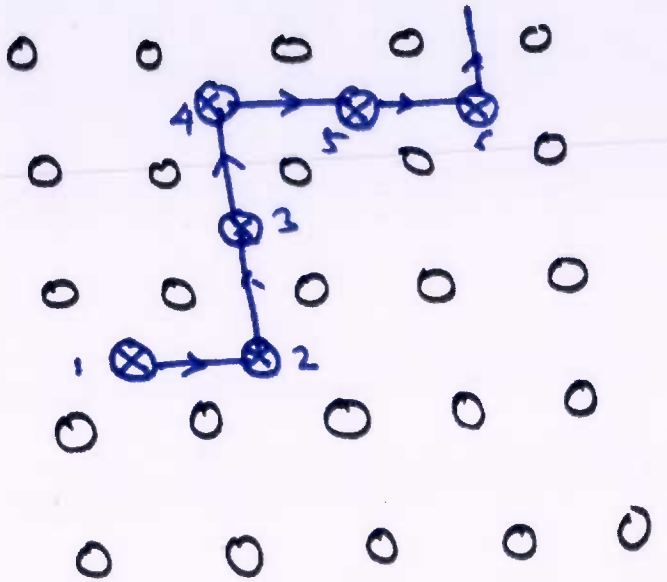
Entropy $S = k \ln(C_{n_f}^{N} \; C_{n_f}^{N'})$. Then doing similar analysis with Gibbs energy function we get

$$n_f = \sqrt{N N'} \; e^{-E_f/2kT}$$

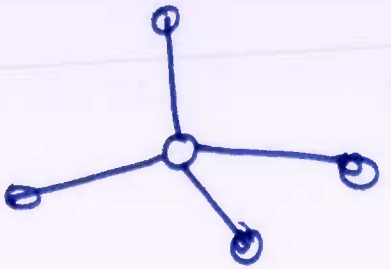
E_f in Si = 1.1 eV

Nature of Diffusion

1. Interstitial Diffusion :



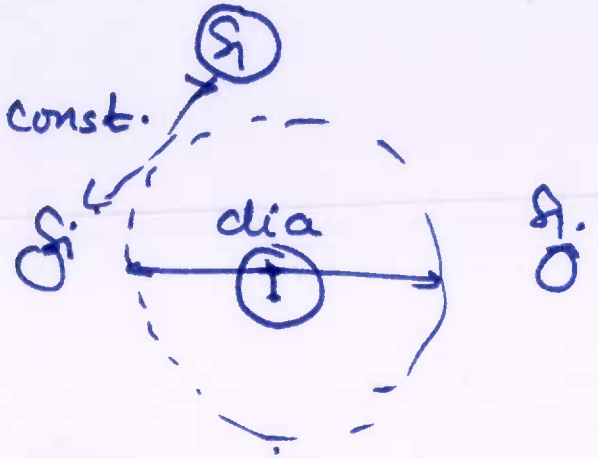
Premitive Lattice of Silicon



Tetrahedral

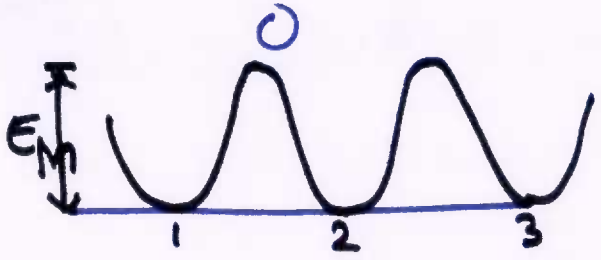
In Silicon Lattice, we understand, there are 5 Voids (Interstitials) arranged Tetrahedrally. Some are occupied, but most are available sites for Impurities

In Silicon diameter of Interstial Void is 2.36 Å and Conslictions are of 2.10 Å



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 occure with frequency ν [f(T)] (Jump f)

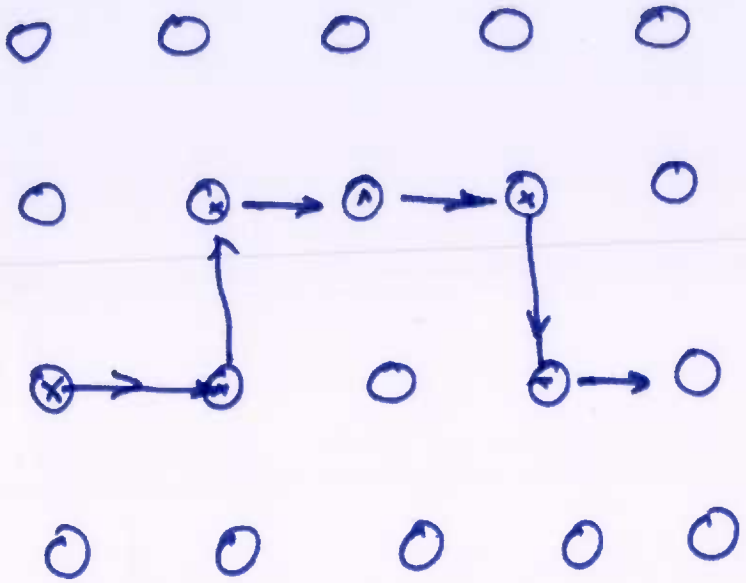


Then $$\nu = 4\nu_0 e^{-E_m/kT}$$

where E_m is Barrier energy. 4 appears due to Degeneracy

Typically Model suggests that $E_M = 1eV$, & 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 <u>Fewer</u> than Such Interstitial Sites, the jump rate of this Diffusion Process is Smaller.