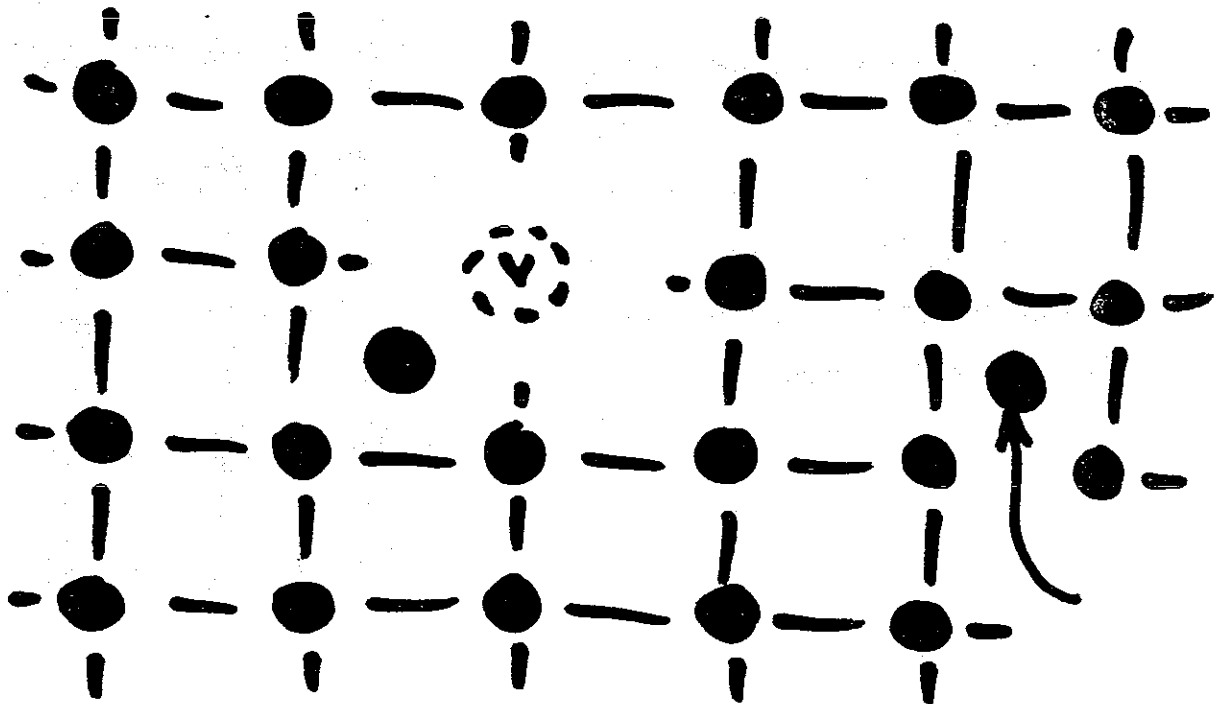


Point Defects

- Defects are any deviation from the perfect, infinite crystal.
- Point defects are defects which limited in size to approximately atomic dimensions.
- There are also line, plane and volume defects which have, respectively, one, two or three dimensions which are significantly greater than the atomic scale.
- An impurity, such as a dopant, can be considered a point defect; however, when we refer to point defects in this class we will generally be referring to intrinsic point defects, interstitials and vacancies, which are present even in pure material.
- In an infinite crystal, point defects can only be created in pairs (Frenkel pairs); however, the existence of surfaces allows the generation of interstitials and vacancies independently (Schottky defects).



Intrinsic point defects are present even under thermal equilibrium. At temperatures above 0°K, there is an equilibrium number of both interstitials and vacancies.

Question: *Why would an ideal lattice form an interstitial at all?*

From thermodynamics, if pressure is constant, the Gibbs Free Energy G tends to be a minimum,

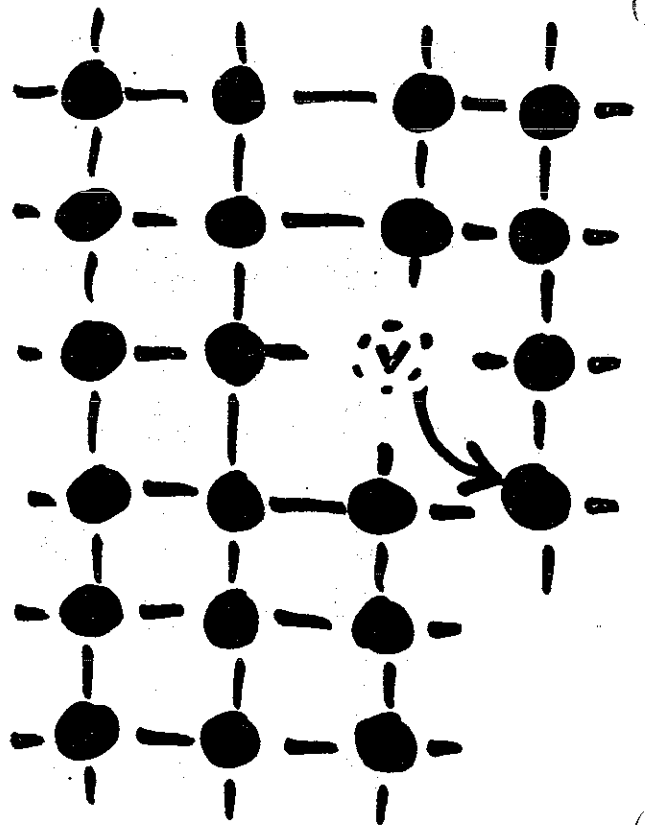
$$G = H - TS \quad (1)$$

The perfect crystal has lowest enthalpy, H . However, entropy S is a measure of disorder; therefore, S increases as the number of defects increases. In general,

$$S = k \ln w, \quad (2)$$

where w is the number of possible arrangements. For a perfect crystal, $w = 1$ and $S = k \ln 1 = 0$.

If a vacancy is generated (by bringing an atom from the bulk to the surface), entropy increases since there are many possible locations for the vacancy, but just one perfect configuration of the crystal.



Next question: *What determines how many vacancies (or interstitials) will be present at equilibrium?*

To answer this question, we minimize the Gibbs Free Energy.

Upon forming a vacancy, the change in free energy of the system is

$$\Delta G_V = \Delta H_V^f - T\Delta S_V \quad (3)$$

We can break up ΔS_V into three parts:

- The entropy of mixing, which depends on the possible number of different possible arrangements of vacancies within the crystal;

$$\Delta S_V^m = k \ln \left[\frac{w(n_V)}{w(n_V - 1)} \right] \quad (4)$$

The number of ways of putting n_V vacancies into N sites is just

$$w(n_V) = \frac{N!}{(N - n_V)!n_V!} \quad (5)$$

so

$$\frac{w(n_V)}{w(n_V - 1)} = \frac{N - n_V + 1}{n_V} = \frac{C_s - C_V}{C_V} \quad (6)$$

where $C_s \equiv$ the concentration of possible defect sites.

- The configuration entropy, which depends on the number of different configurations of the vacancy θ_V is just

$$\Delta S_V^c = k \ln \theta_V \quad (7)$$

- The remaining entropy change due to different vibrational modes, etc. We will call this the formation energy, ΔS_V^f .

The total entropy change is the sum of the three terms,

$$\Delta S_V = \Delta S_V^m + \Delta S_V^c + \Delta S_V^f$$

Setting ΔG_V to zero,

$$\Delta H_V^f - T(\Delta S_V^m + \Delta S_V^c + \Delta S_V^f) = \Delta H_V^f - T\Delta S_V^f - kT \ln \left[\frac{\theta_V(C_s - C_V)}{C_V} \right] = 0 \quad (8)$$

Therefore, in equilibrium

$$\frac{C_V^*}{C_s - C_V^*} = \theta_V \exp \left(-\frac{\Delta H_V^f - T\Delta S_V^f}{kT} \right) \quad (9)$$

More generally, we can consider an arbitrary defect X:

$C_X \equiv$ concentration of sites occupied by a defect

$C_s - C_X \equiv$ concentration of defect sites without a defect (unoccupied sites)

$C_X^* \equiv$ equilibrium defect concentration

$$\frac{C_X^*}{C_s - C_X^*} = \theta_X \exp \left(\frac{-\Delta G_X^f}{kT} \right) \quad (10)$$

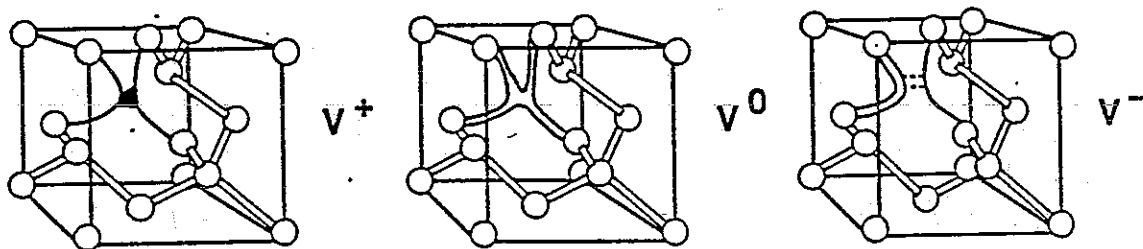
$$\Delta G_X^f = \Delta H_X^f - T\Delta S_X^f \quad (11)$$

For dilute solutions (most cases), $C_X \ll C_s$ so

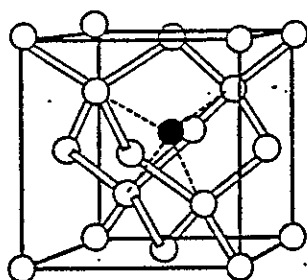
$$C_X^* \cong \theta_X C_s \exp \left(\frac{-\Delta G_X^f}{kT} \right) \quad (12)$$

Point Defect Structures

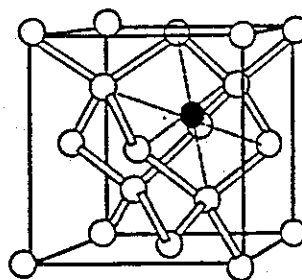
The structure of a silicon vacancy is reasonably well-characterized.



There remains considerable debate over the structure of the silicon interstitial. Originally, it was thought that the interstitial would occupy one of the largest open spaces in the lattice.

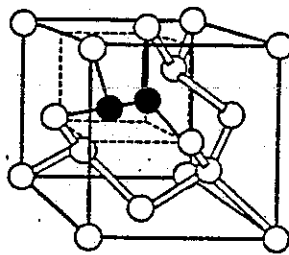


**Tetrahedral
Interstitial**

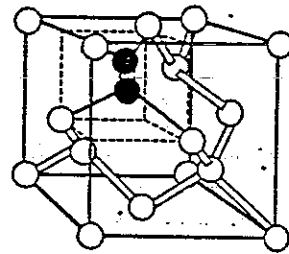


**Hexagonal
Interstitial**

More recent calculations have shown that the interstitial interacts strongly sharing electrons with the rest of the lattice. Possible configurations are for two atoms to share a single lattice site.

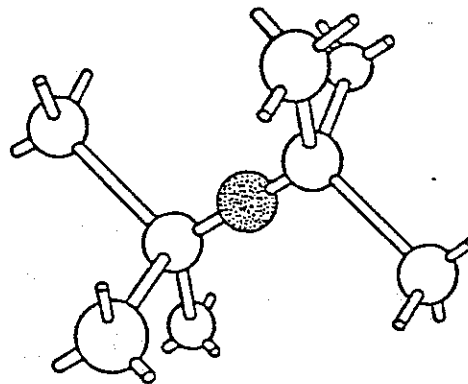


$(Al)^0$, acceptor
 I^+



$(Al)^-$, acceptor
 I^0
 $(Al)^+$, donor

Or for the extra atom to sit in the bond-centered site.



The equilibrium structure may depend on the charge state.

For most of our analysis, the precise structure of point defects does not the modeling of fabrication processes.

Charged Point Defects

Like other deviations from the ideal crystal (impurities, surfaces, etc.), native point defects have charge states within the band-gap. That means they can take on electrons or holes and become charged. For example, a neutral defect X^0 can become negatively charged by taking on an electron.



The ratio of numbers in the different charge states just depends on the differences in the free energy of formation since we assume that electronic processes (charging reactions) are fast enough to keep up with the much slower processes of chemical reactions and diffusion.

$$\frac{C_{X^-}}{C_{X^0}} = \frac{\theta_{X^-}}{\theta_{X^0}} \left[\frac{\exp\left(\frac{-\Delta G_{X^-}^f}{kT}\right)}{\exp\left(\frac{-\Delta G_{X^0}^f}{kT}\right)} \right] = \frac{\theta_{X^-}}{\theta_{X^0}} \exp\left(-\frac{\Delta G_{X^-} - \Delta G_{X^0}}{kT}\right) \quad (2)$$

We can also think of the reaction in terms of the change in energy of the electron upon becoming captured. The expected value of the energy of an electron removed from (or added to) the conduction and valence bands is just the Fermi level (E_f), and E_{X^-} is the energy of the extra electron that makes the defect negatively charged.

The relative numbers of defects in each of the charge states can therefore be written in terms of the Fermi level location.

$$\frac{C_{X^-}}{C_{X^0}} = \frac{\theta_{X^-}}{\theta_{X^0}} \exp\left(-\frac{E_{X^-} - E_f}{kT}\right) \quad (3)$$

The ratio of the number of configurations accounts for the fact that with unpaired electrons there is a spin degeneracy of 2 (spin could be + or -).

Similarly, it is possible for defects to take on additional electrons, becoming (more negatively charged).



$$\frac{C_{X=}}{C_{X^0}} = \frac{C_{X=} C_{X^-}}{C_{X^-} C_{X^0}} \quad (5)$$

$$\frac{C_{X=}}{C_{X^0}} = \frac{\theta_{X=}}{\theta_{X^0}} \exp\left(-\frac{E_{X=} + E_{X^-} - 2E_f}{kT}\right) \quad (6)$$

Eventually, the energy required to add an extra electron will be above the conduction band minimum and can be neglected since they will generally remain unoccupied. Similarly, point defects can capture holes (emit electrons) to become positively charged.

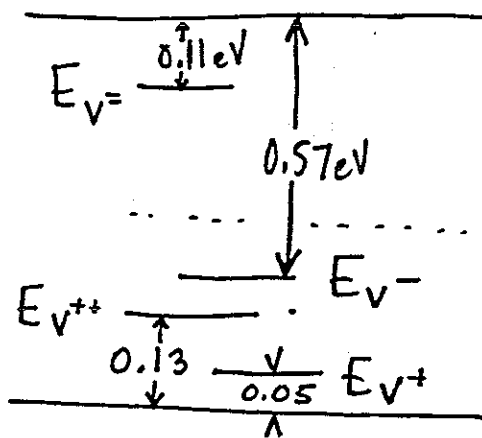
$$\frac{C_{X^+}}{C_{X^0}} = \frac{\theta_{X^+}}{\theta_{X^0}} \exp\left(-\frac{E_f - E_{X^+}}{kT}\right) \quad (7)$$

$$\frac{C_{X^{++}}}{C_{X^0}} = \frac{\theta_{X^{++}}}{\theta_{X^0}} \exp\left(-\frac{2E_f - E_{X^{++}} - E_{X^+}}{kT}\right) \quad (8)$$

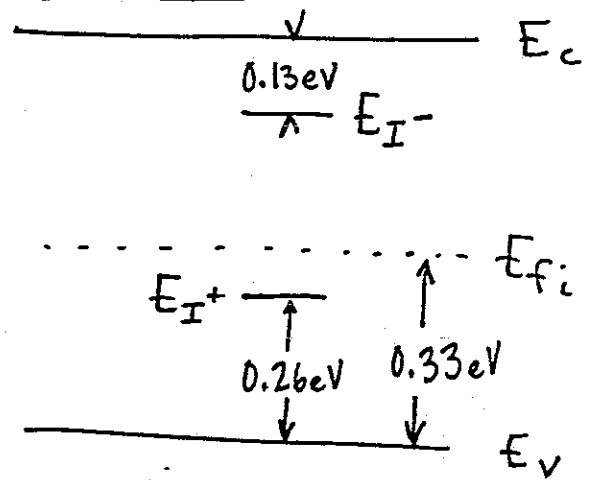
For vacancies, it is believed that the singly- and doubly-negative and singly- and doubly-positive states all exist within the band-gap, while for interstitials, only the singly-charged levels are thought to be within the band-gap.

Estimated location of charge states for vacancies and interstitials

Vacancies



Interstitials



1000°C

Note: Usually, the second ionization energy is higher, i.e. it's harder to remove the second electron. But for the silicon vacancy, the doubly-positive level $E_{V^{++}}$ is closer to E_c so it has a lower ionization energy than V^+ . This is an unusual property and V^{++} is known as a "negative- U " defect.

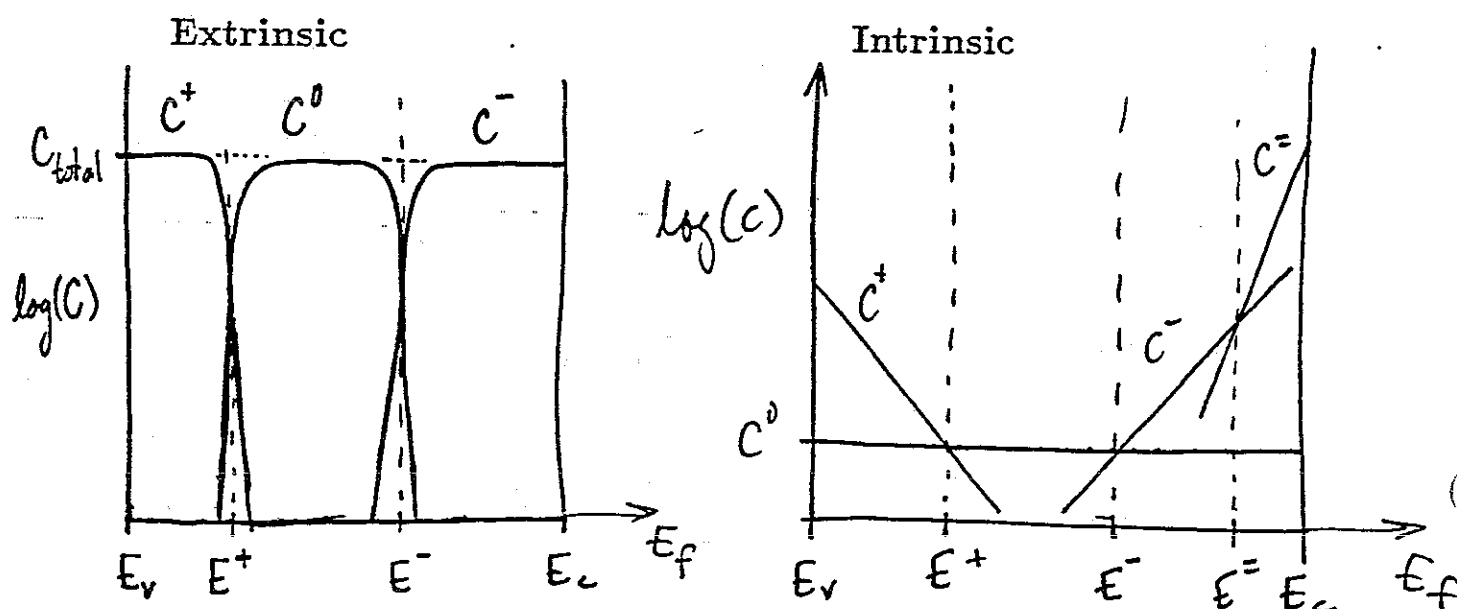
For the extrinsic defects (like dopants), the total number of defects is fixed so that as the Fermi level changes the relative numbers of defects in different charge states changes, but the total number remains fixed by the composition.

$$N_{total} = N_{X^-} + N_{X^0} + N_{X^+} \quad (9)$$

Thus for $E_f \uparrow$, $N_{X^-}/N_{X^0} \downarrow$, $N_{X^-} \uparrow$, $N_{X^0} \downarrow$

Intrinsic point defects are different in that every lattice site is a potential point defect. Thus if a defect becomes negatively charged, another defect can be generated to replace it.

In addition, the equilibrium number of neutral defects is independent of the Fermi level since they are uncharged. Therefore, as the Fermi level is shifted, the total number of point defects changes, not just the relative numbers.



The relative occupation of the defect charge states can also be expressed in terms of the electron concentration since they both have the same dependence on the Fermi level position.

$$\frac{C_{X^-}}{(C_{X^-})_i} = \exp\left(\frac{E_f - E_{fi}}{kT}\right) = \frac{n}{n_i} \quad (10)$$

where the i subscript indicates in intrinsic material where $n = n_i$.

This is also apparent from basic chemistry. The law of mass-action says that for any reaction,



in equilibrium,

$$C_A C_B = K(T) C_C \quad (12)$$

where $K(T)$ is a temperature-dependent equilibrium constant.

Thus for electron capture by a defect,



$$nC_{X^0} = K(T) C_{X^-} \quad (14)$$

in equilibrium (which we assume for the charging reactions as noted earlier).

Similarly, for other charge states,

$$\frac{C_{X=}}{(C_{X=})_i} = \left(\frac{n}{n_i}\right)^2 \quad (15)$$

$$\frac{C_{X+}}{(C_{X+})_i} = \frac{p}{n_i} = \frac{n_i}{n} \quad (16)$$

$$\frac{C_{X++}}{(C_{X++})_i} = \left(\frac{p}{n_i}\right)^2 = \left(\frac{n_i}{n}\right)^2 \quad (17)$$

Thus, the total defect concentration in equilibrium can be written:

$$C_X = (C_{X^0}^*) + (C_{X^-}^*)_i \left(\frac{n}{n_i}\right) + (C_{X=}^*)_i \left(\frac{n}{n_i}\right)^2 + (C_{X^+}^*)_i \left(\frac{n}{n_i}\right)^{-1} + (C_{X^{++}}^*)_i \left(\frac{n}{n_i}\right)^{-2} \quad (18)$$

Bandgap Narrowing

An additional complication that enters at high temperatures and in heavily-doped material is band-gap narrowing.

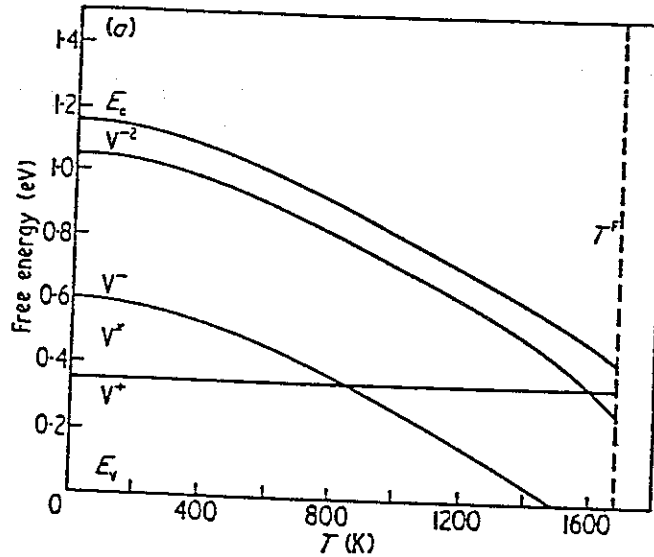
$$E_g \cong E_{g0} - \beta T \quad (19)$$

More accurately,

$$E_g = E_{g0} - \beta \left(\frac{T^2}{T + 636} \right) \quad (20)$$

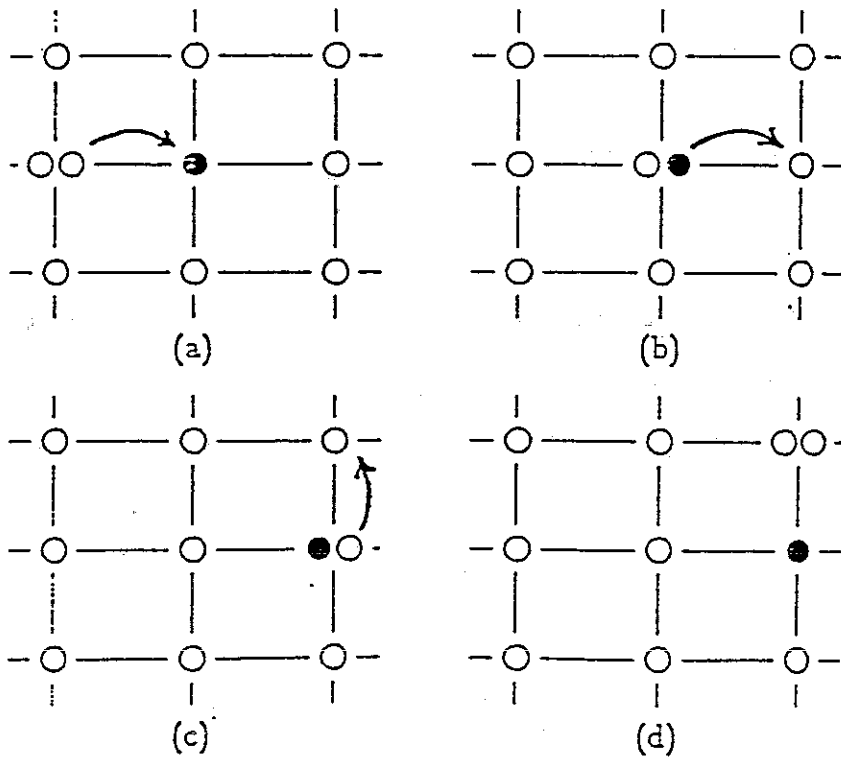
where $E_{g0} = 1.17\text{eV}$, $\beta = 4.73 \times 10^{-4}\text{eV}/^\circ\text{K}$.

Van Vechten has claimed (although it is still controversial) that the acceptor states remain at a fixed distance from the conduction band and the donor states remain at a fixed distance from the valence band as the gap narrows so that at high temperature, the charged defect states are more dominant than at lower temperatures.

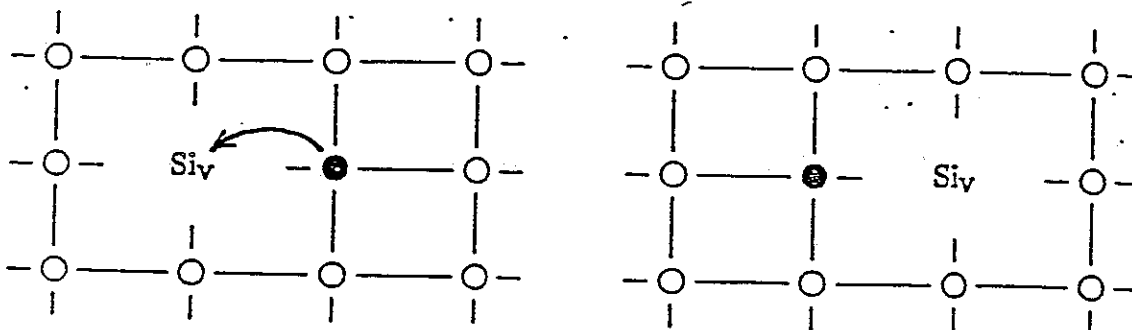


Migration of Point Defects

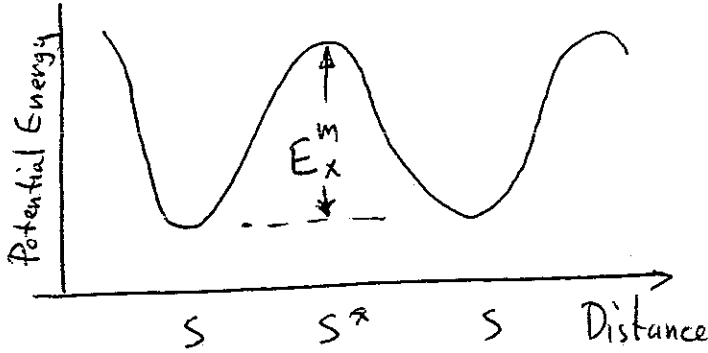
Point defects move by hopping between their lowest energy sites.



For vacancies, it is the other surrounding atoms that move, but as for holes, it is easier to think of the movement of the empty sites.



To move, point defects must gain the saddle-point energy, which can be divided into enthalpy and entropy terms.



$$E_X^m = H_X^m - TS_X^m \quad (1)$$

As for chemical kinetics in general, the rate of a process such as hopping depends on attempt frequency ν^0 and activation barrier.

The jump frequency ν_X^m is given by:

$$\nu_X^m = \nu^0 \exp\left(\frac{-E_X^m}{kT}\right) \quad (2)$$

which can be rewritten as

$$\nu_X^m = \nu^0 \exp\left(\frac{S_X^m}{k}\right) \exp\left(\frac{-H_X^m}{kT}\right) \quad (3)$$

The attempt frequency ν^0 is generally only a weak function of temperature ($\sim 10^{13}\text{sec}^{-1}$).

From a macroscopic perspective, the result of random hopping on a lattice leads to diffusion as described by Fick's Law.

$$J_X = -d_X \nabla C_X \quad (4)$$

where J_X is the material flux.

Since $\partial C / \partial t = \nabla \cdot J$, considering only diffusion we arrive at a simple continuity equation.

$$\frac{\partial C_X}{\partial t} = d_X \nabla^2 C_X \quad (5)$$

The diffusivity is proportional to the hopping frequency

$$d_X = \lambda^2 \nu_X^m / 6 \quad (6)$$

where λ is the hop distance (distance between minima).

The diffusivity thus can be written

$$d_X = d_X^0 \exp(-Q_X/kT) \quad (7)$$

and d_X^0 and Q_X can be determined by plotting experimental data with the log of the diffusivity versus $1/T$ (called an Arrhenius plot).

Experimental values for vacancies generated via radiation at low temperatures (70-220°K) give $Q_V = H_V$ in the range of 0.1 to 0.45 eV, dependent on charge state.

The total point defect flux requires summing over all the charge states so

$$J^T = \sum_i J_{X^i} = d_X^{\text{eff}} \frac{\partial C_X^T}{\partial x} \quad (8)$$

where i represents the charge state, $C_X^T = \sum_i C_{X^i}$, and

$$d_X^{\text{eff}} = \sum_i d_{X^i} \frac{C_{X^i}}{C_X^T} \quad (9)$$

The fraction of defects in each of the charge states depends on the location of the levels in the gap and the Fermi level location (or electron concentration or doping level).

Silicon Self Diffusion

Self-diffusion is the diffusion of silicon in silicon. It can be measured by monitoring the movement of silicon isotopes (tracers) or inferred from metal diffusion studies.

A typical result is

$$D_{\text{self}} = 1400 \exp\left(-\frac{5.01 \text{ eV}}{kT}\right) \quad (10)$$

Silicon self-diffusion arises from the motion of point defects so that

$$D_{\text{Si}} = (\phi_{\text{I}} + 1) d_{\text{I}}^{\text{eff}} \frac{C_{\text{I}}}{C_{\text{s}}} + (\phi_{\text{V}} + 1) d_{\text{V}}^{\text{eff}} \frac{C_{\text{V}}}{C_{\text{s}}} \quad (11)$$

where the ϕ 's are correction factors due to non-random jumping (correlation coefficients).

It is clear from Equation (11) that it is the product of defect concentration times defect diffusivity ($D_{\text{X}}C_{\text{X}}$) which determines the rate of self diffusion.

If one mechanism is dominant (either interstitials or vacancies of a specific charge state) then self diffusion would be expected to show an Arrhenius dependence.

$$D_{\text{Si}} = D_{\text{Si}}^0 \exp(-Q_{\text{Si}}/kT) \quad (12)$$

with

$$Q_{\text{Si}} = H_{\text{X}}^{\text{f}} + H_{\text{X}}^{\text{m}} \quad (13)$$

and

$$D_{\text{Si}}^0 = \theta_{\text{X}}(\phi_{\text{X}} + 1) d_{\text{X}}^0 \exp\left(\frac{S_{\text{X}}}{k}\right) \quad (14)$$

The activation energy of self-diffusion includes both the formation and migration barriers.

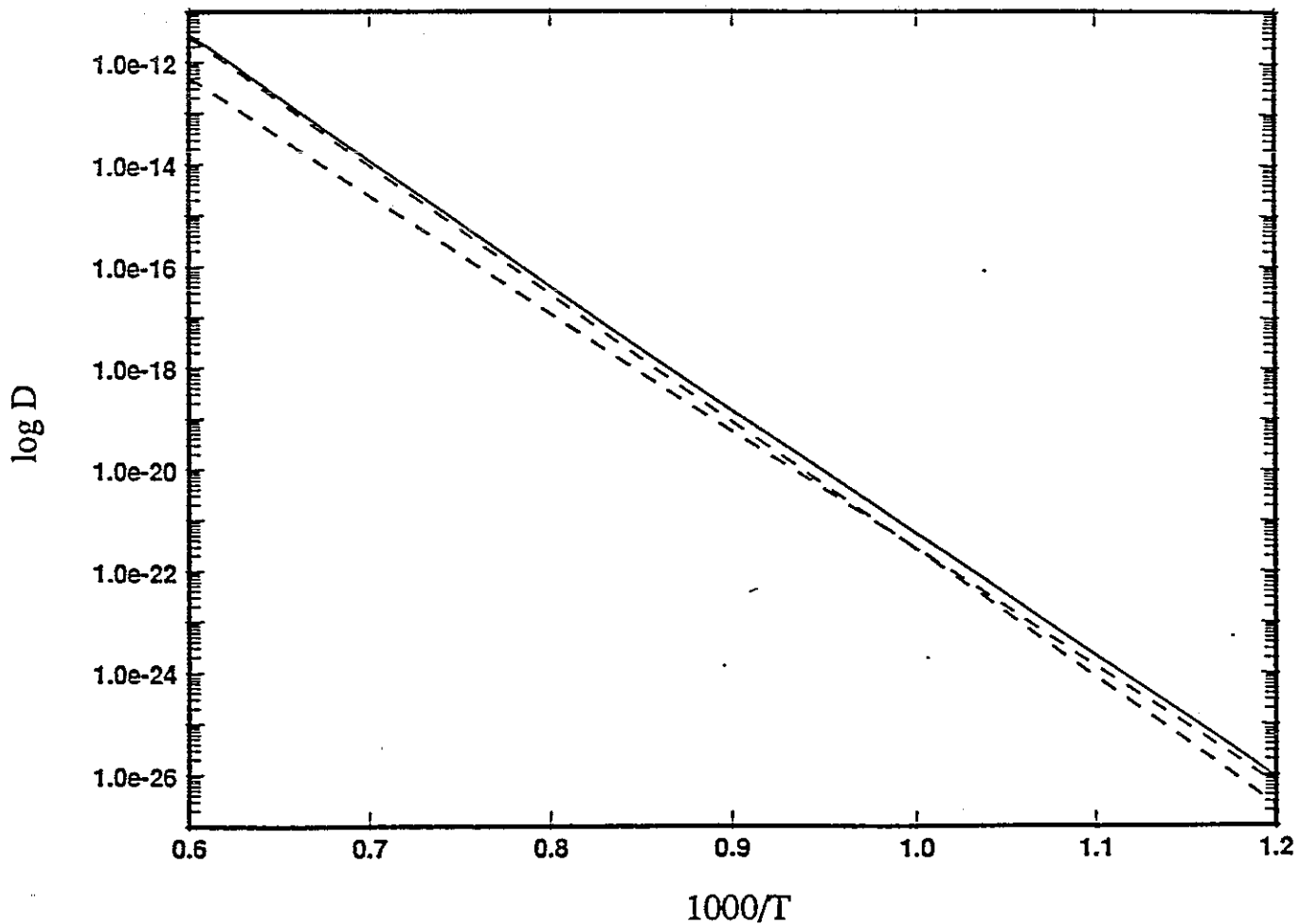
The preexponential terms often calculated from experiment have been used to suggest that defect formation and/or migration is accompanied by substantial lattice relaxations.

The experimental data does generally follow an Arrhenius relationship, but larger activation energies are found at higher temperatures. It has been suggested that interstitials dominate at higher temperatures and vacancies at lower temperatures, with the sum of the two mechanisms giving the total self-diffusion.

$$D_{SiI} = 4000 \exp\left(-\frac{5 \text{ eV}}{kT}\right) \quad (15)$$

$$D_{SiV} = 40 \exp\left(-\frac{4.6 \text{ eV}}{kT}\right) \quad (16)$$

$$D_{Si} = D_{SiI} + D_{SiV} \quad (17)$$



Since the concentrations of point defects increase in extrinsically-doped material, the self-diffusion coefficient does also.

For example, considering positively and negatively charged as well as neutral interstitials,

$$d_I^{\text{eff}} C_I = (d_{I^0} C_{I^0}) + (d_{I^-} C_{I^-}) + (d_{I^+} C_{I^+}) \quad (18)$$

The total self-diffusion coefficient as a function of doping level can then be written as:

$$D_{\text{Si}} = D_{X^0} + \frac{n}{n_i} D_{X^-} + \left(\frac{n}{n_i} \right)^2 D_{X=} + \frac{n_i}{n} D_{X^+} + \left(\frac{n_i}{n} \right)^2 D_{X^{++}} \quad (19)$$

where, for example,

$$D_{X^-} = \frac{1}{C_s} [(1 + \phi_{V^-}) C_{V^-} d_{V^-} + (1 + \phi_{I^-}) C_{I^-} d_{I^-}] \quad (20)$$