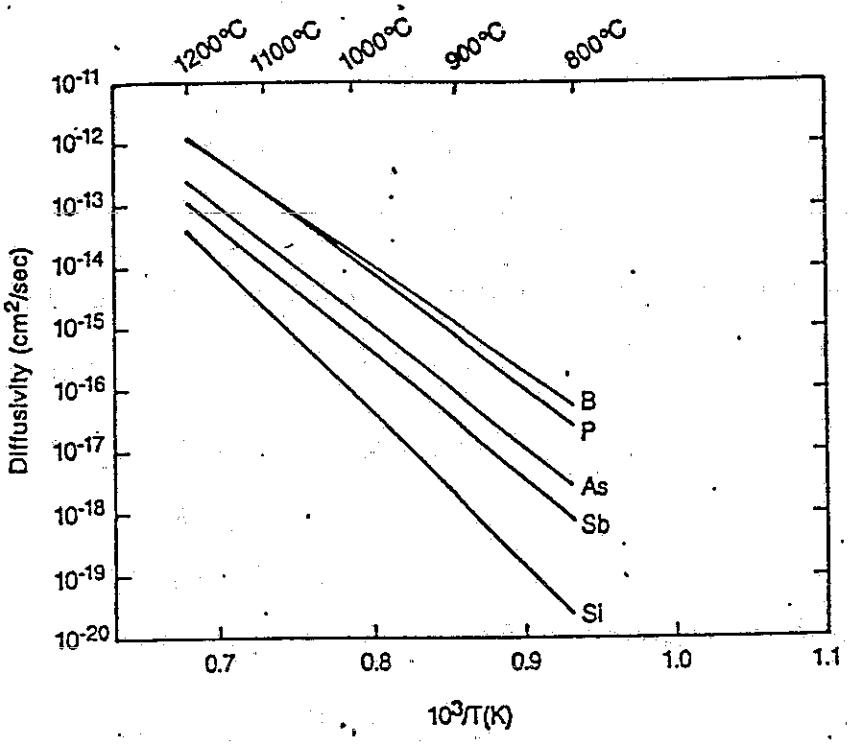
Dopant Diffusion

The diffusivities of substitutional dopants are all much larger than silicon self-diffusion.



Reason: The dopants are attracted to the point defects and thus preferentially displace dopant atoms.

As for self-diffusion,

$$D_{\mathrm{A}} = D_{\mathrm{A}}^{0} \exp(-Q_{\mathrm{A}}^{m}/kT) \tag{1}$$

but $Q_{\mathrm{A}}^{m} < Q_{Si}^{m}$

Dopant diffusion can be thought of as occuring through the formation of dopant/defect pairs and the diffusion of those pairs.

$$\mathrm{A} + \mathrm{X} \Leftrightarrow \mathrm{AX} \tag{2}$$

where A is a dopant and X is a defect.

When dopants are in substitutional sites they are usually active, but they may or may not be active when they combine with a defect.

$$A^+ + X^- \Leftrightarrow (AX)^0 \tag{3}$$

Not electrically active.

$$A^+ + X^0 \Leftrightarrow (AX)^+ \tag{4}$$

Net positive charge – electrically active.

From mass action, if the pairing reaction (Equation (2)) is near equilibrium (thought to be valid under most conditions), the concentration of pairs is

$$C_{\mathrm{AX}} = K(T) C_{\mathrm{A}} C_{\mathrm{X}} \tag{5}$$

$$K(T) = \frac{\theta_{\mathrm{AX}}}{C_S} \exp\left(\frac{E^b_{\mathrm{AX}}}{kT}\right) \tag{6}$$

There are four nearest neighbors, so $\theta_{AV} = 4$

$$C_{\mathrm{AX}} = \frac{\theta_{\mathrm{AX}} C_A C_{\mathrm{X}}}{C_S} \exp\left(\frac{E^b_{\mathrm{AX}}}{kT}\right) \tag{7}$$

From experiment, $E^b_{\mathrm{PV}} \geq 1.04eV$

$E^b_{\mathrm{AsV}} \geq 1.23eV$

$E^b_{\mathrm{SbV}} \geq 1.44eV$

$E^b_{\mathrm{BiV}} \geq 1.64eV$

Note: We have used the dilute solution approximation.

$$\frac{C_{\mathrm{AX}}}{C_{\mathrm{X}}} = \theta_{\mathrm{AX}} \frac{C_A}{C_S} \exp\left(\frac{E^b_{\mathrm{AX}}}{kT}\right) \tag{8}$$

The dilute solution approximation allows us to use C_A/C_S on the right hand side instead of $C_A/(C_S - C_A)$.

The pair binding energy which be due both Coulombic interactions and lattice distortion interactions

- For the Coulombic interaction,

$$E^b_{\text{coul}} = \frac{q_1 q_2}{\epsilon_{\text{Si}} r} \tag{9}$$

  which gives a binding energy of about 0.5eV for singly-charged species brought to nearest neighbor sites.

  All of the dopant/vacancy binding energies exceed the Coulomb potential.

- For lattice distortion, would expect large atom (Sb,As) to be attracted to vacancy, forming vacancy pairs and small atoms (B,P) to form interstitial pairs.

  As expected for vacancies, binding energy increases with increasing size, but even for phosphorus which is about the same size as silicon, there appears to be attraction beyond the Coulomb interaction.

Note that dopant/interstitial pair can either be dopant and silicon atoms sharing single site or dopant in interstitial or bond-centered site.

From modeling perspective the two cases are indistinguishable – interstitial dopant atom has dopant **and** interstitial (extra atom) attributes.

The flux of dopants is just the flux of pairs,

$$J_{\mathrm{A}} = -\left[d_{\mathrm{AV}}\frac{\partial C_{\mathrm{AV}}}{\partial x} + d_{\mathrm{AI}}\frac{\partial C_{\mathrm{AI}}}{\partial x}\right] \tag{10}$$

For low doping (intrinsic), $n = n_i$ and $E_f = E_{fi}$. Thus, the relative concentrations of species are constant and in equilibrium

$$\frac{C_{\mathrm{AX}}}{C_{\mathrm{A}}} = K(T)C_{\mathrm{X}}^{*} \tag{11}$$

which is a function only of T.

Thus,

$$\frac{\partial C_{\mathrm{AX}}}{\partial x} = \left(\frac{C_{\mathrm{AX}}}{C_{\mathrm{A}}}\right)\frac{\partial C_{\mathrm{A}}}{\partial x} \tag{12}$$

$$J_{\mathrm{A}} = -\left[d_{AV}\left(\frac{C_{AV}}{C_{\mathrm{A}}}\right)\frac{\partial C_{\mathrm{A}}}{\partial x} + d_{AI}\left(\frac{C_{AI}}{C_{\mathrm{A}}}\right)\frac{\partial C_{\mathrm{A}}}{\partial x}\right] \tag{13}$$

$$J_{\mathrm{A}} = -\left[D_{AV}\frac{\partial C_{\mathrm{A}}}{\partial x} + D_{AI}\frac{\partial C_{\mathrm{A}}}{\partial x}\right] \tag{14}$$

Concentration of defects is the same everywhere and, there are no electric fields in the material so there is no drift, only diffusion. Therefore, $D_{\mathrm{A}} = D_{AV} + D_{AI}$

The result is normal Fickian diffusion, with solutions that are sums of Gaussians (impulse response).

Now let's go to the extrinsic case, $n > n_i$ (net donor doping).

- Relative occupation of charge states changes.
  - Concentration of neutral defects and dopants unchanged.
  - More negatively charged defects.
  - More neutral and negative pairs ($A^+X^- \equiv (AX)^0$).

    If the pairing reaction is near equilibrium,

$$\frac{C_{(AX)^0}}{C_{A^+}} = KC_{X^-} = KC^i_{X^-}\left(\frac{n}{n_i}\right) \tag{15}$$

- Electric fields.

  When the electron concentration changes due to doping, there is a built-in electric field induced.

$$\mathcal{E} = -\frac{kT}{q}\nabla\left[\ln\left(\frac{n}{n_i}\right)\right] = -\frac{kT}{q}\left(\frac{n_i}{n}\right)\nabla\left(\frac{n}{n_i}\right) \tag{16}$$

  When the electronic processes are near equilibrium (as we will generally assume), the electron concentration can be written in terms of the doping density

$$\left(\frac{n}{n_i}\right) = \frac{N_d^+ - N_a^-}{2n_i} + \sqrt{\left(\frac{N_d^+ - N_a^-}{2n_i}\right)^2 + 1} \tag{17}$$

Including electric-field effects, the pair flux for any single charge state can then be written as diffusion plus drift terms:

$$J_{(AX)^i} = -d_{(AX)^i}\frac{\partial C_{(AX)^i}}{\partial x} + Z_{(AX)^i}\mu_{(AX)^i}C_{(AX)^i}\mathcal{E} \tag{18}$$

If the defect concentrations remain near their equilibrium values, the continuity equation for the dopant:

$$\frac{\partial C_A}{\partial t} = \frac{\partial \sum_i J_{(AX)^i}}{\partial x} \tag{19}$$

can be rewritten in terms of the doping concentration only, eliminating the pair concentrations. The result is a concentration or Fermi-level dependent dopant diffusivity.

This model (called the Fermi model) finds broad application and is the default model in SUPREM IV.

The basic assumptions are:

1. Dopants diffuse via dopant/defect pairs.
2. The pairing reactions are near equilibrium
3. Both defects and pairs exist in a number of charge states.
4. Electronic processes remain near equilibrium
   (a) The relative numbers of defects and pairs in the different charge states are as in equilibrium.
   (b) $pn = n_i^2$
5. Charge neutrality.
6. The defect concentrations are near their equilibrium values.

The Fermi model does a good job of accounting for diffusion of all dopants at low ($n < n_i$) and moderate ($n \sim n_i$) concentrations.

The Fermi model also is generally successful for antimony (Sb) and arsenic (As).

Phosphorus (P) and to a lesser extent boron (B) show more complicated behavior as we will discuss later.

Single Species Diffusion

If there is only one dopant diffusing, Equation (19) can be written in a very simple form:

$$\frac{\partial C_{\mathrm{A}}}{\partial t} = D_{\mathrm{A}} \frac{\partial^2 C_{\mathrm{A}}}{\partial x^2} \tag{20}$$

The one difference from standard Fickian diffusion is that the diffusivity is a function of the doping concentration.

As an example, for acceptors (A^-) assuming they pair only with X^0, X^+, and X^{++}.

$$D_{\mathrm{A}} = h\left[D^i_{\mathrm{A}\text{-}\mathrm{X}^0} + D^i_{\mathrm{A}\text{-}\mathrm{X}^+}\left(\frac{p}{n_i}\right) + D^i_{\mathrm{A}\text{-}\mathrm{X}^{++}}\left(\frac{p}{n_i}\right)^2\right] \tag{21}$$

$$h = \left[1 + \frac{C_{A^-}/2n_i}{\sqrt{(C_{A^-}/2n_i)^2 + 1}}\right] \tag{22}$$

The derivation of this expression is left to the homework.

The electric field factor for a single diffusing dopant (h) has the following properties:

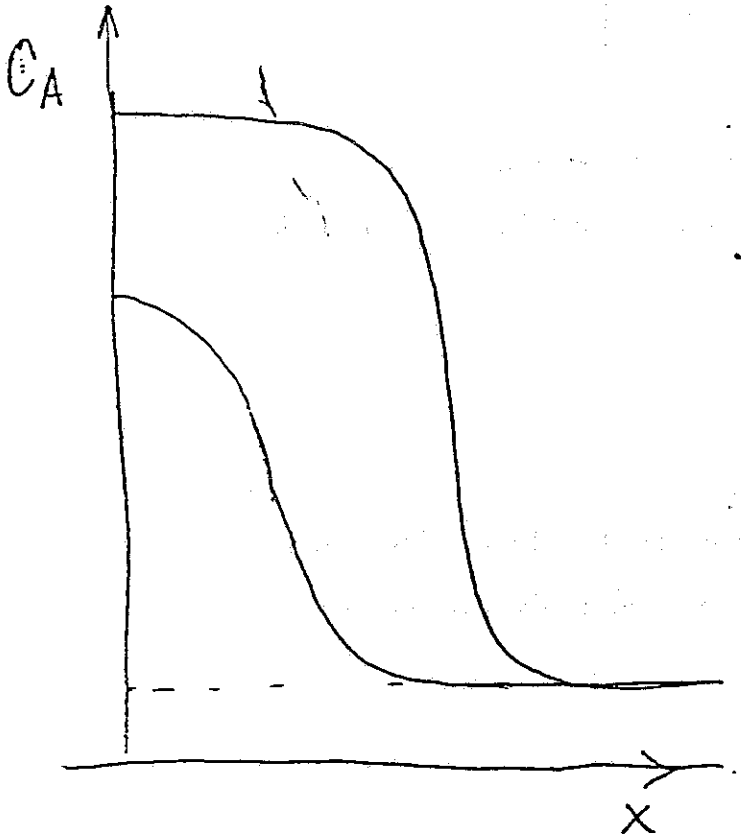
- $h = 1$ if $C_{A^-} << n_i$ (low doping)
- $h = 2$ if $C_{A^-} >> n_i$ (high doping)

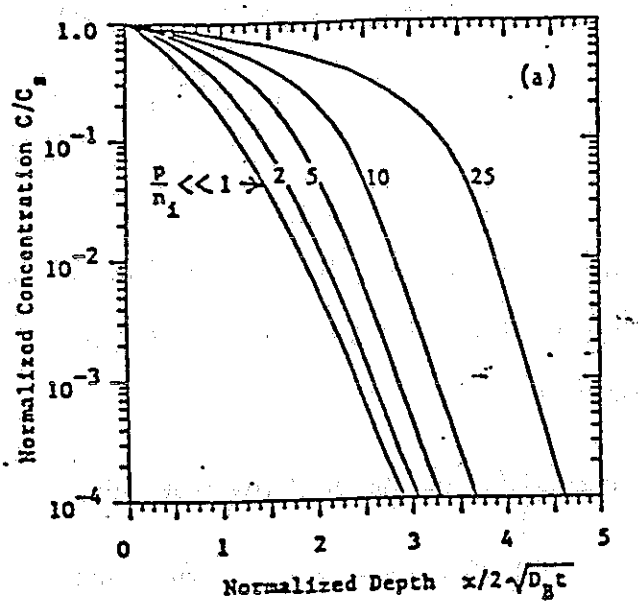
  The factor of two is due to the same effect that reduces the base transit time under high level injection due to the electric field enhancement.

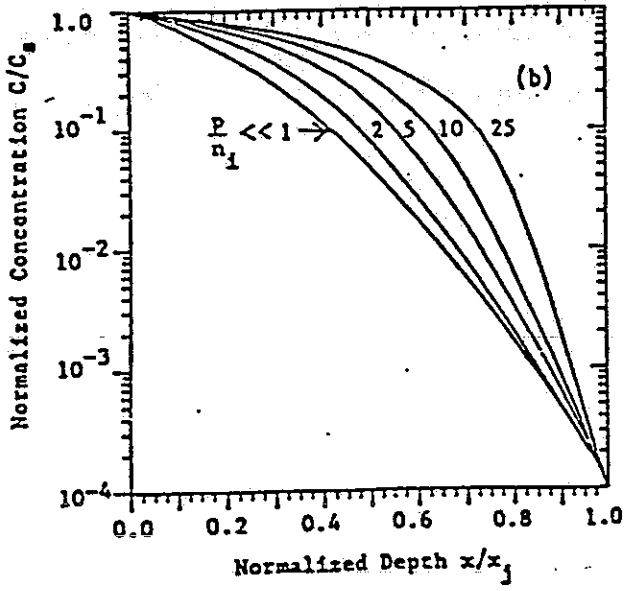
The simple form of Equation (21) is due to the fact that the straight electric field enhancement term for negatively charged pairs (diffusion with neutral defects) which modifies the first term is exactly the same as the correction due to the concentration of neutral pairs being proportional to (n/n_i) for the second term.

For the positively-charged pairs, the concentration is proportional to $(n/n_i)^2$, giving a correction which compensates for the drift induced in the opposite direction, with the net correction again the same.

Diffusion is faster in the heavily-doped portion of the profile giving rise to profiles which are more square-shaped than the standard erfc or Gaussian profiles arising from constant diffusivity.







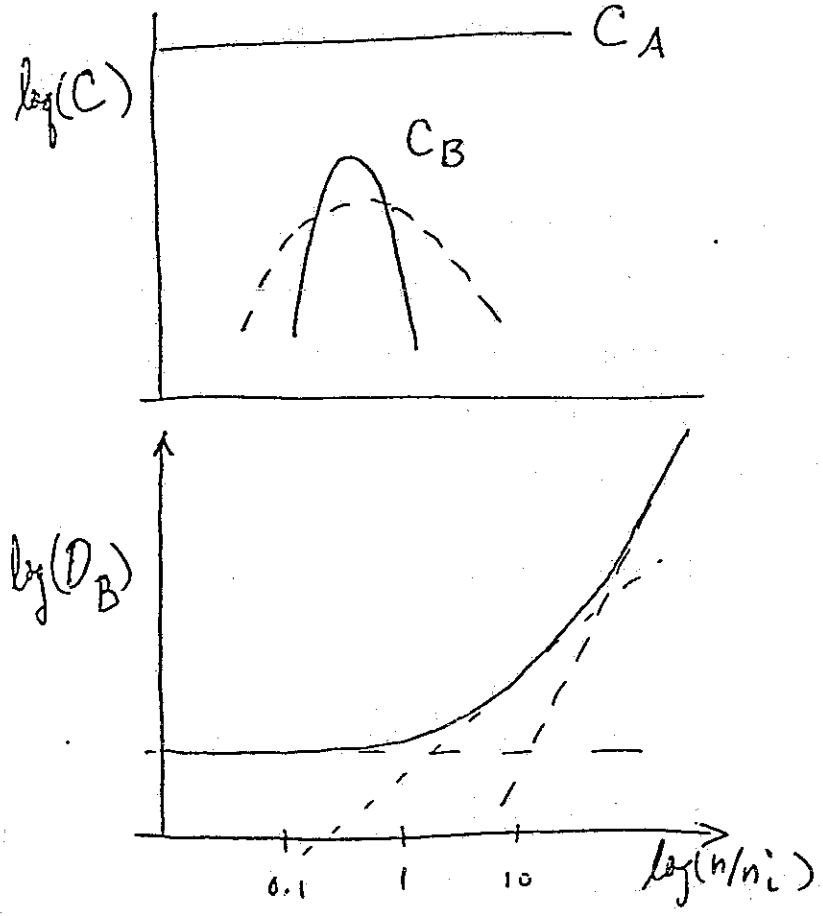
Multiple species diffusion

In integrated circuits, multiple species are diffusing simultaneously.

An easily-analyzed case is when one dopant diffuses in a high constant background of another dopant.

In this case, the Fermi level is constant and there are no electric fields or gradients in the electron concentration, so the resulting continuity equation is as for a single dopant, but with $h = 1$.

This type of system is very useful for charactering point defect interactions with dopant diffusion since electric field effects are removed and the diffusivity is constant over the whole profile.



Experiments using this structure are called iso-concentration experiments and can be used to calculate $D^i_{A\text{-}X^0}$, $D^i_{A\text{-}X^+}$, etc.

Generally, high donor doping enhances the diffusion of other donors (more negatively-charged defects) and retards the diffusion of acceptors (fewer positively-charged defects which diffuse with acceptors).

For the general case, the drift term cannot be combined with the diffusion term since the electric field no longer depends on the the gradient in $\ln(C)$.

Instead, separate drift and diffusion terms are required:

$$\frac{\partial C_{\mathrm{A}}}{\partial t} = D_{\mathrm{A}} \left[\frac{\partial^2 C_{\mathrm{A}}}{\partial x^2} - \frac{q Z_{\mathrm{A}}}{kT} \frac{\partial (\mathcal{E} C_{\mathrm{A}})}{\partial x} \right] \tag{23}$$

The electric field then depends on the net doping concentration, not just the concentration of the diffusing species alone.

Interesting effects can result from co-diffusion of two species.

Example: Ga (acceptor) and As

Some of the interactions:

- Slow diffusion of Ga in heavily-doped As region.
  - $E_f \Uparrow$, C_{X^+}, $C_{\mathrm{X}^{++}} \Downarrow$, $C_{\mathrm{Ga\text{-}X}^+}$, $C_{\mathrm{Ga\text{-}X}^{++}} \Downarrow$,
  - Possibly $(\mathrm{As}^+/\mathrm{Ga}^-)$ pairing.
- Dip in Ga concentration.
  - $\mathcal{E}$-field effects.
  - To left of junction, As^+ gradient causes flux of Ga^- to left.
  - To right of junction, Ga^- gradient causes flux of Ga^- to right.

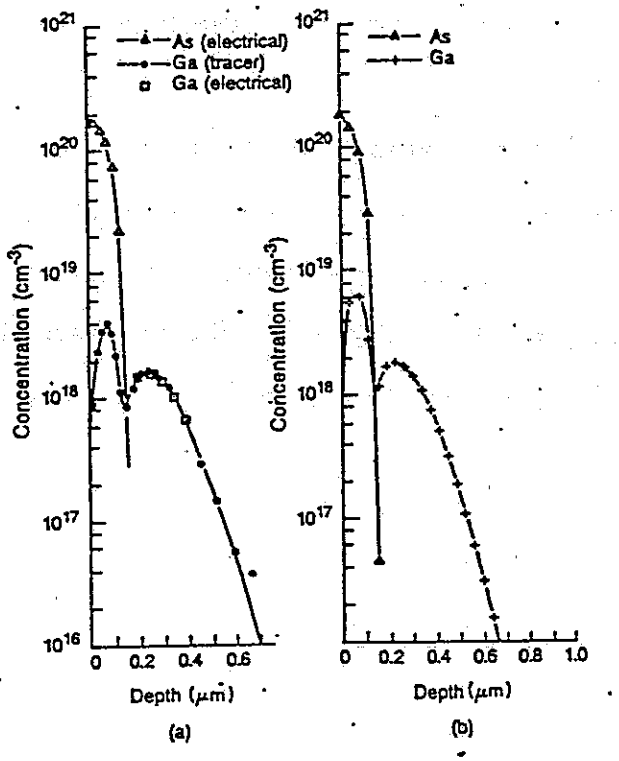


FIG. 12. Codiffusion of a donor dopant As and acceptor dopant Ga: (a) experimental result; (b) simulated result using the formalism of Appendix A. From Mallam, Jones, and Willoughby (1981).