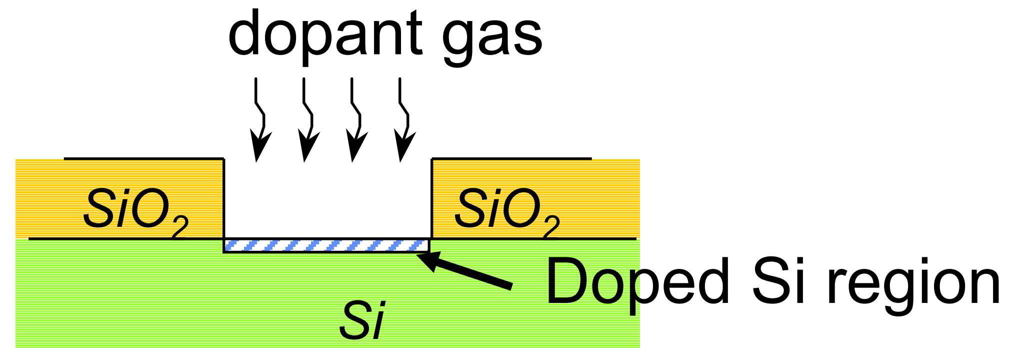
Dopant Diffusion

(1) Predeposition

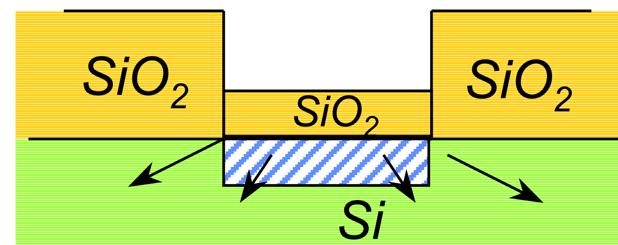
dose control



(2) Drive-in

Turn off dopant gas
or seal surface with oxide

profile control
(junction depth;
concentration)

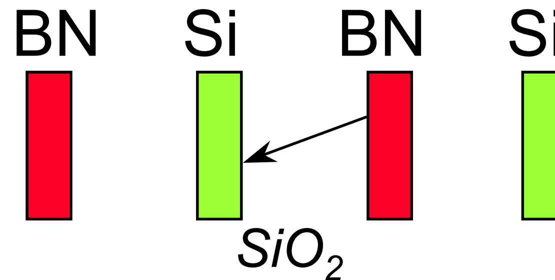


Note: Predeposition by diffusion can also be replaced by a shallow implantation step.

Dopant Diffusion Sources

(a) Gas Source: AsH_3, PH_3, B_2H_6

(b) Solid Source



(c) Spin-on-glass SiO_2+dopant oxide

(d) Liquid Source.

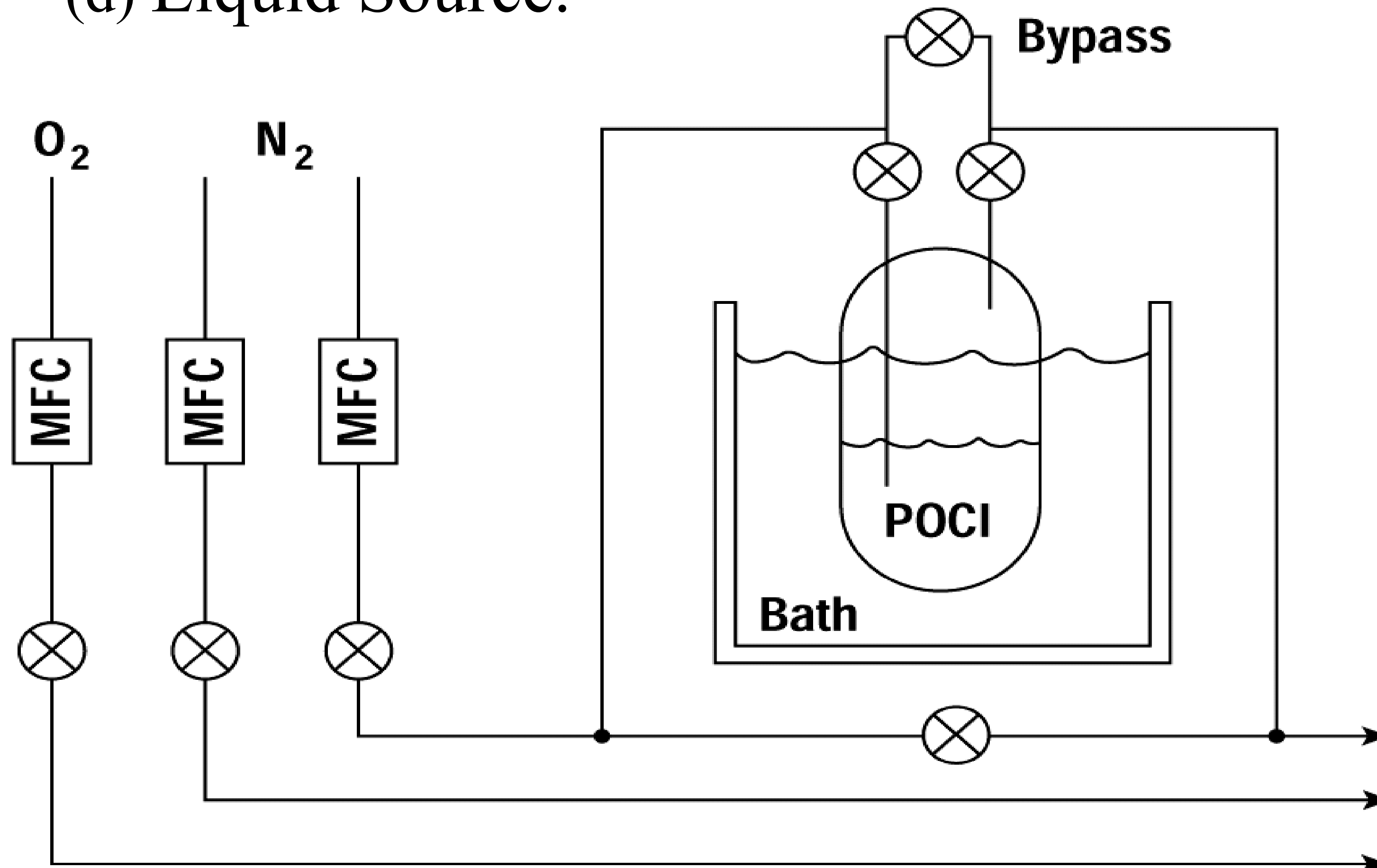
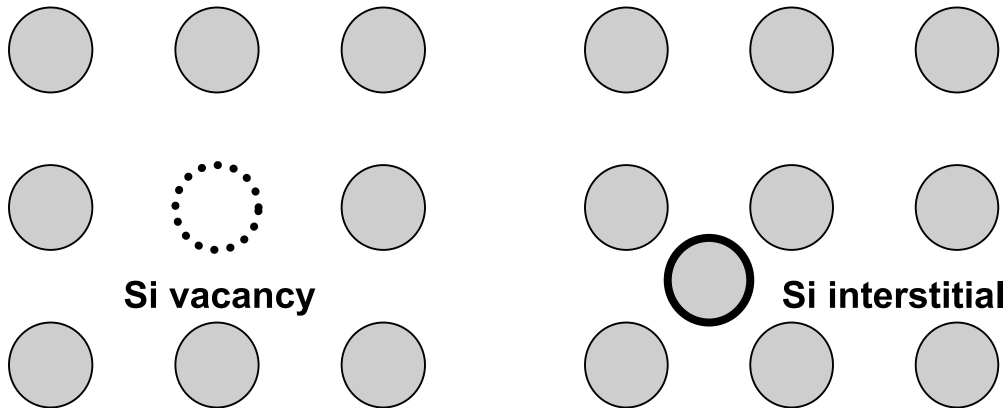


Figure 3.20 A typical bubbler arrangement for doping a silicon wafer using a POCl source. The gas flow is set using mass flow controllers (MFC).

Si Native Point Defects

For reference only



1) Thermal-equilibrium values of Si *neutral* interstitials and vacancies at diffusion temperatures << doping concentration of interest (10^{15} – 10^{20} /cm^3)

$$C^*_{I^0} \cong 1 \times 10^{27} \exp\left(\frac{-3.8 \text{ eV}}{kT}\right)$$

$$C^*_{V^0} \cong 9 \times 10^{23} \exp\left(\frac{-2.6 \text{ eV}}{kT}\right)$$

At 1000°C, $C_{Io}^* \sim 10^{12}$ /cm3
$C_{Vo}^* \sim 10^{13}$ /cm3

2) Diffusivity of Si interstitials and Si vacancies >> diffusivity of dopants

$$d_I = 1.58 \times 10^{-1} \exp\left(-\frac{1.37}{kT}\right) \text{cm}^2 \text{ sec}^{-1}$$

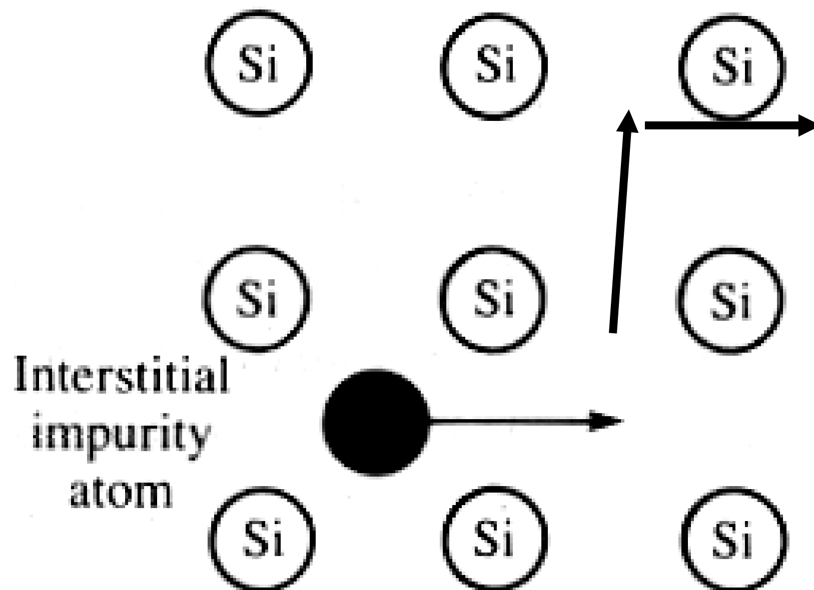
$$d_V = 1.18 \times 10^{-4} \exp\left(-\frac{0.1}{kT}\right) \text{cm}^2 \text{ sec}^{-1}$$

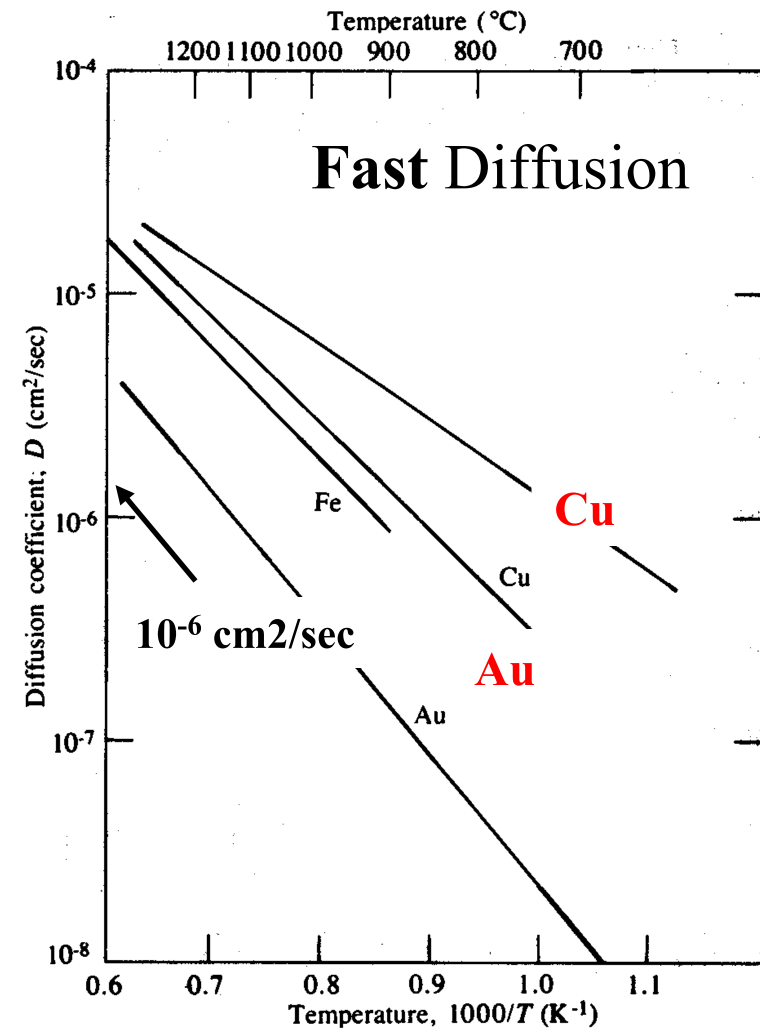
Diffusion Mechanisms in Si

(A) No Si Native Point Defect Required

Example: Cu, Fe, Li, H

(a) Interstitial Diffusion



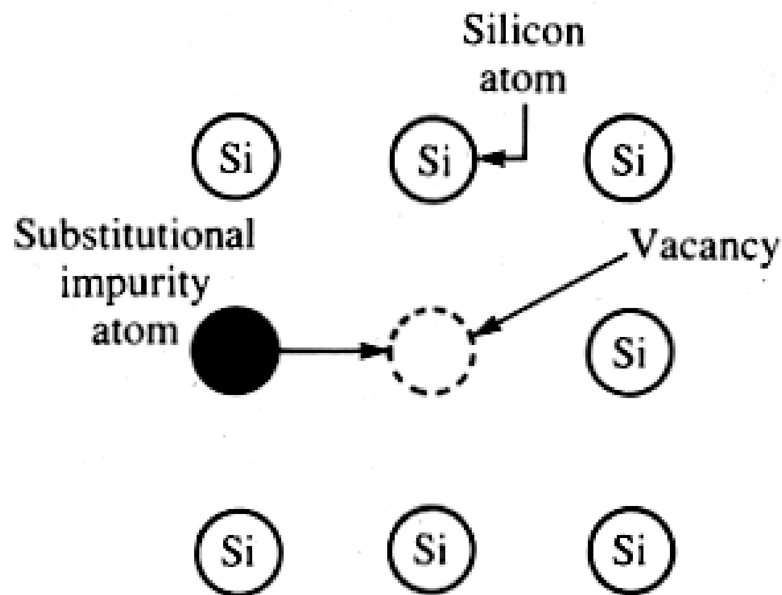


Diffusion Mechanisms in Si

(B) Si Native Point Defects Required (Si vacancy and Si interstitials)

Example: Dopants in Si (e.g. B, P,As,Sb)

(a) Substitutional Diffusion



(b) Interstitialcy Diffusion

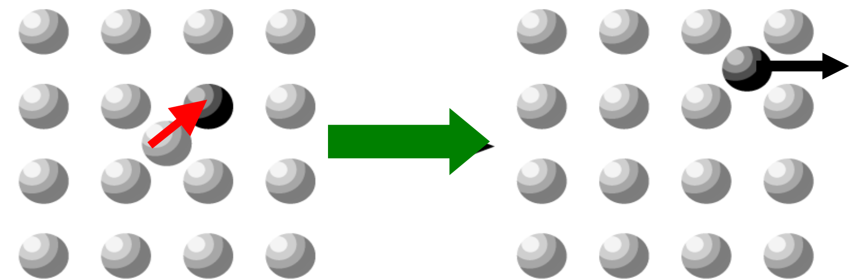


Figure 3.5 In interstitialcy diffusion an interstitial silicon atom displaces a substitutional impurity, driving it to an interstitial site where it diffuses some distance before it returns to a substitutional site.

(B) Si Native Point Defects Required (Si vacancy and Si interstitials) continued

(c) Kick-Out Diffusion
(d) Frank Turnbull Diffusion

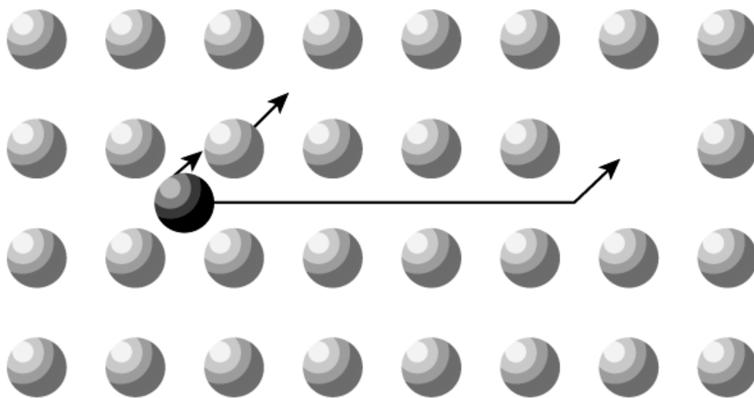
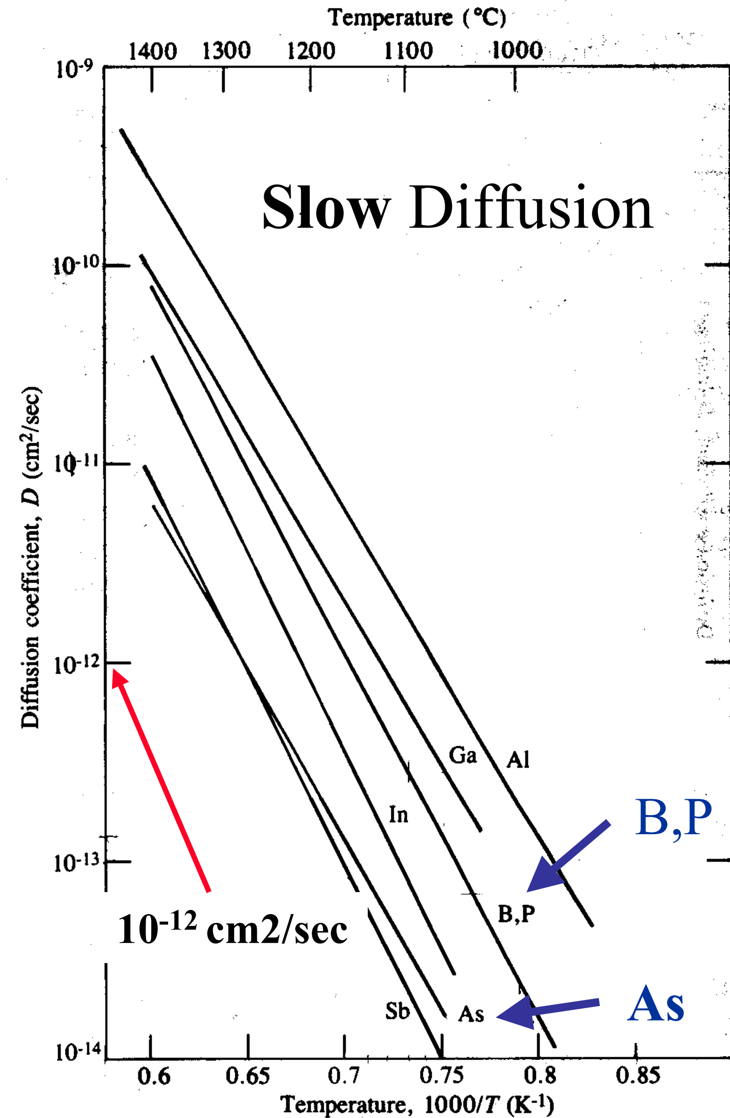
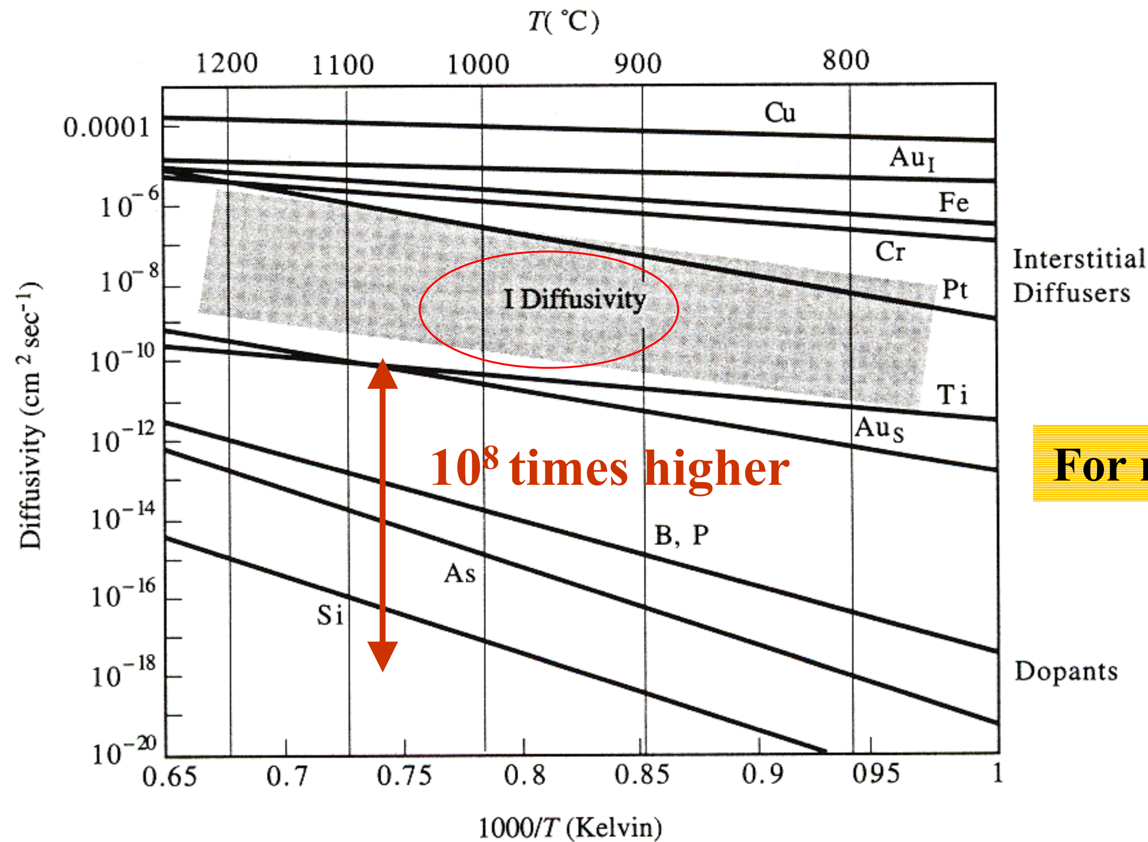


Figure 3.6 The kick-out (left) and Frank–Turnbull mechanisms (right).



Diffusivity Comparison:

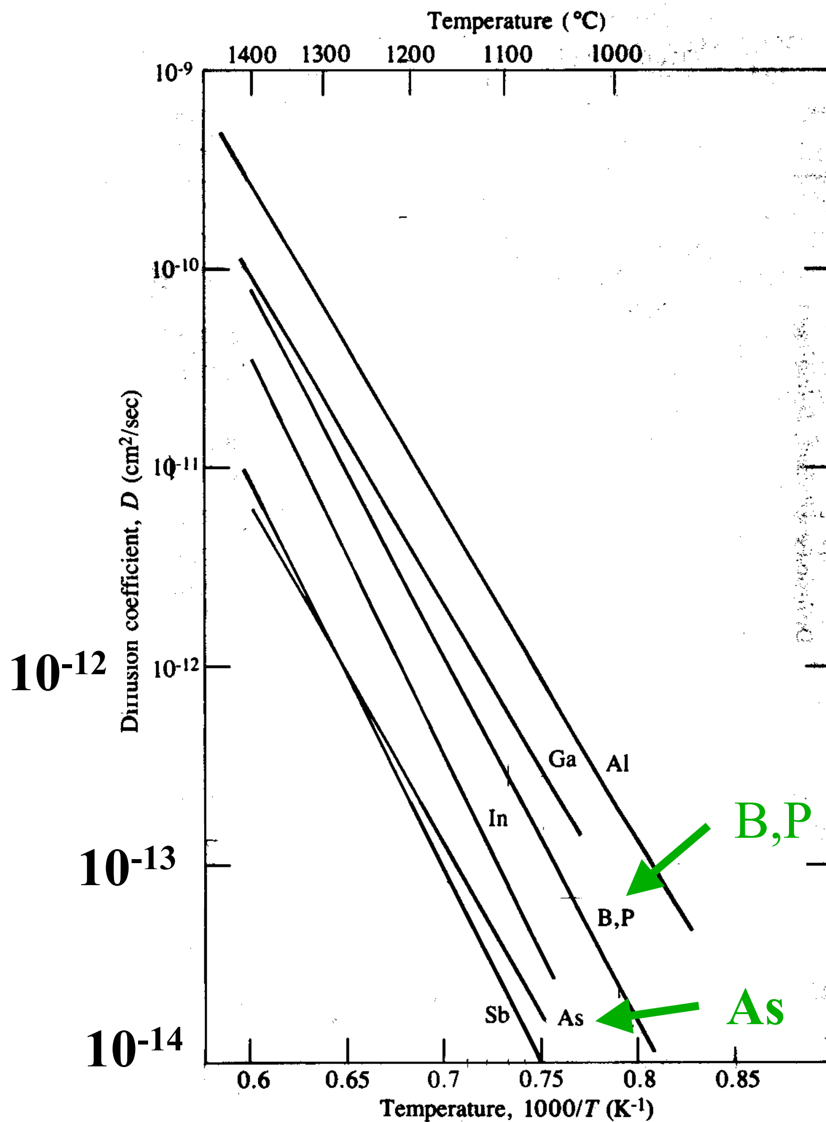
Dopants, Si interstitial, and interstitial diffusers

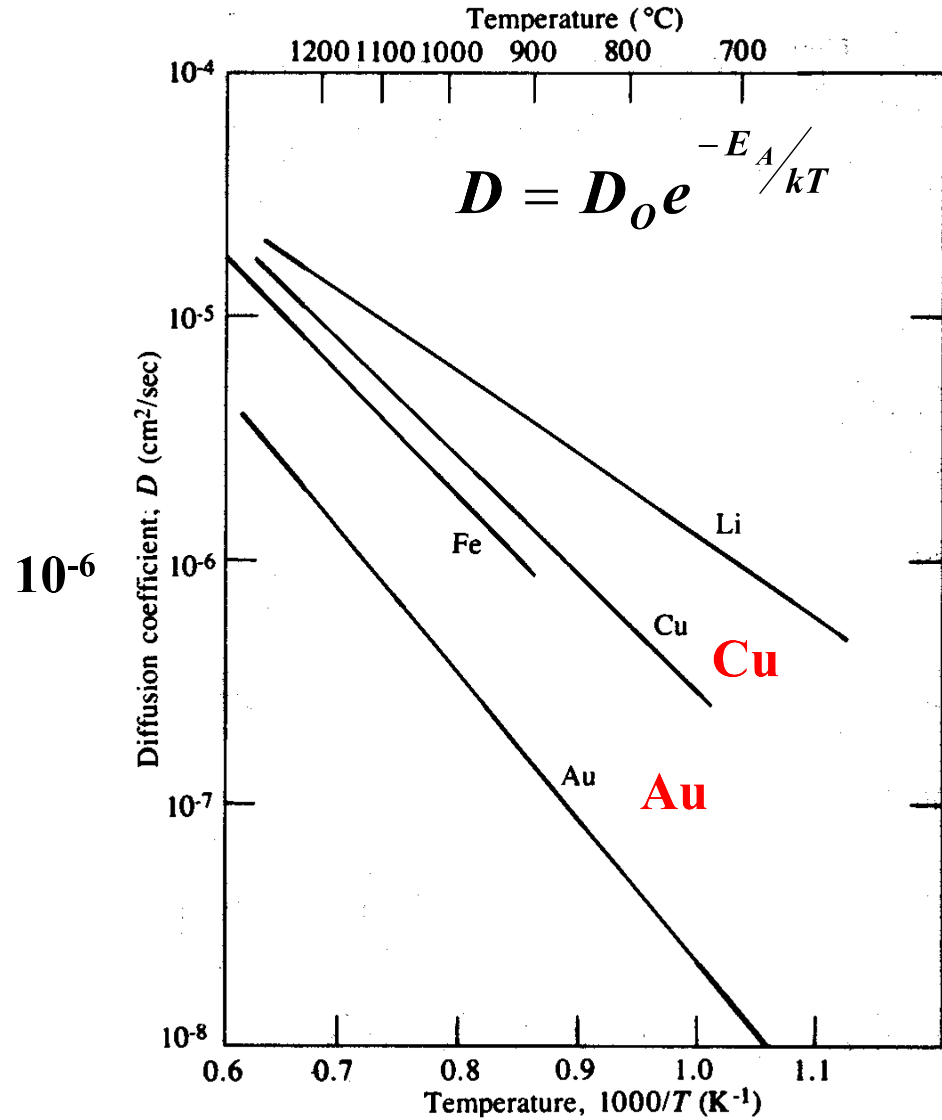


For reference only

Figure 4–8 Diffusivities of various species in silicon. Au_S refers to gold in substitutional form (on a lattice site); Au_I to gold in an interstitial site. The silicon interstitial (I) diffusivity is also shown and will be discussed later. The gray area representing the I diffusivity indicates the uncertainty in this parameter. (After [4.10, 4.11].)

Diffusion Coefficients of Impurities in Si





Temperature Dependence of D

$$D = D_0 e^{-E_A/kT}$$

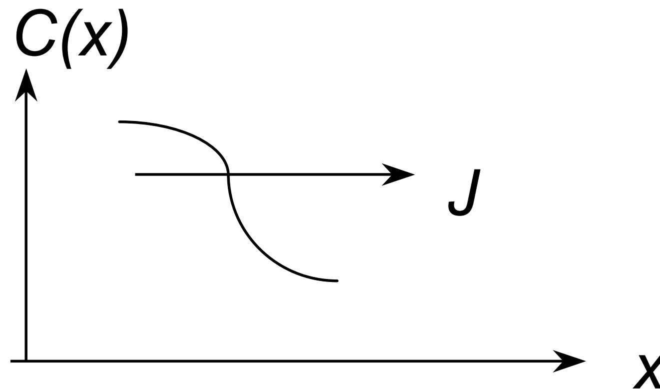
E_A = activation energy in eV

k = Boltzman constant

$= 8.6 \times 10^{-5}$ eV / kelvin

D_0, E_A are tabulated.

Mathematics of Diffusion



Fick's First Law:

$$J(x,t) = -D \cdot \frac{\partial C(x,t)}{\partial x}$$

$$D : diffusion \quad constant$$

$$[D] = cm^2 / \sec$$

From the Continuity Equation

$$\frac{\partial C(x,t)}{\partial t} + \nabla \cdot J(x,t) = 0$$

$$\Rightarrow \frac{\partial C(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x} = \frac{\partial}{\partial x}\left(D\frac{\partial C(x,t)}{\partial x}\right)$$

$$\Rightarrow \boxed{\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C(x,t)}{\partial x}\right)}$$

"Diffusion Equation"

Concentration independence of D

If D is independent of C
(i.e., D is independent of x).

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

Concentration Independent Diffusion Equation

State of the art devices use fairly high concentrations, causing variable diffusivity and other significant side-effects (transient-enhanced diffusion, for example.)

Solid Solubility of Common Impurities in Si

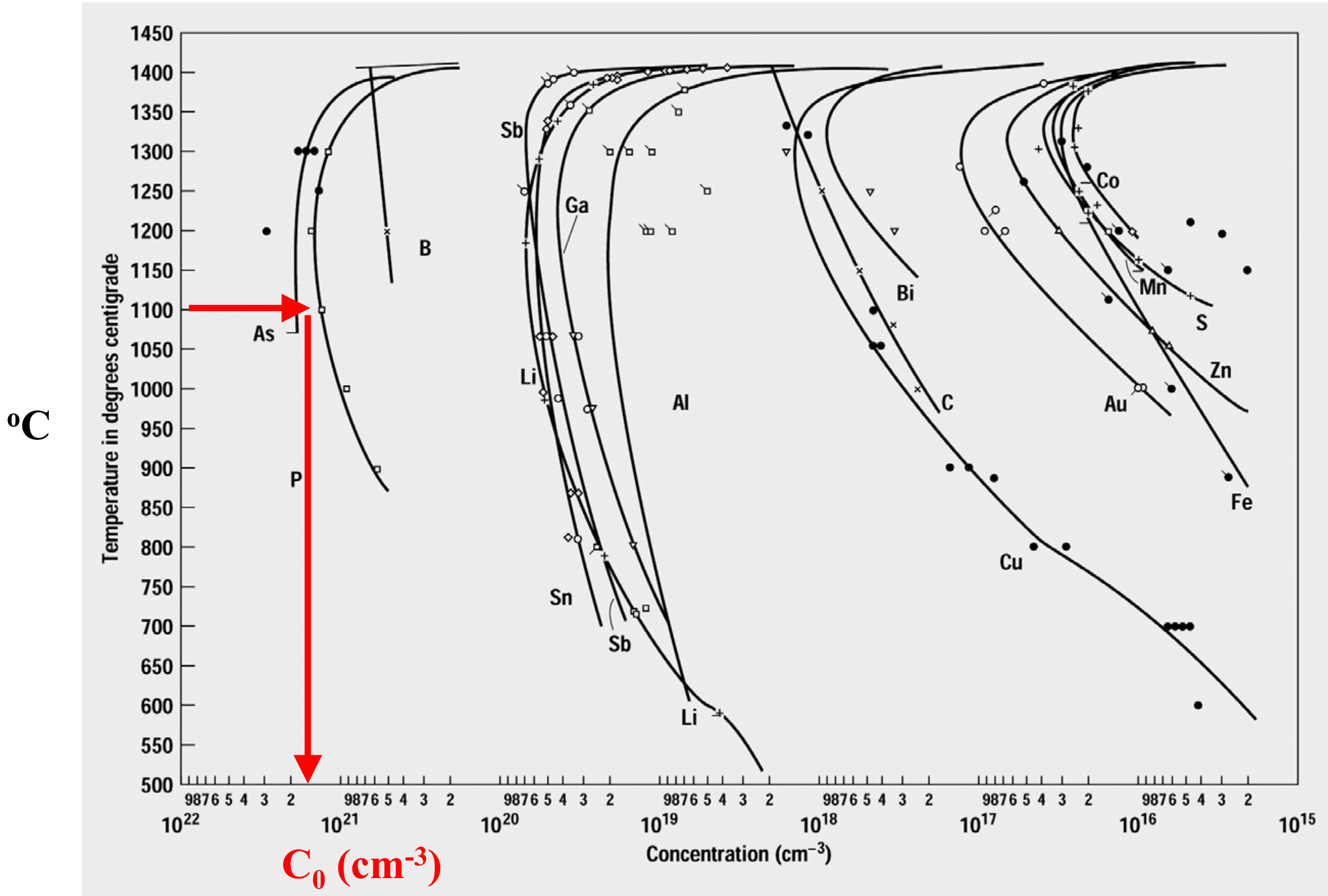


Figure 2.4 Solid solubility of common silicon impurities *(all rights reserved, reprinted with permission, © 1960 AT & T).*

A. Predeposition Diffusion Profile

$$\bullet \textit{Boundary Conditions:}$$

$$C(x=0,t) = C_0 = \textit{solid solubility of the dopant}$$

$$C(x=\infty,t) = 0$$

Justification:
Si wafers are ~500um thick, doping depths of interest are typically < several um

$$\bullet \textit{Initial Condition:}$$

$$C(x,t=0) = 0$$

At time =0, there is no diffused dopant in substrate

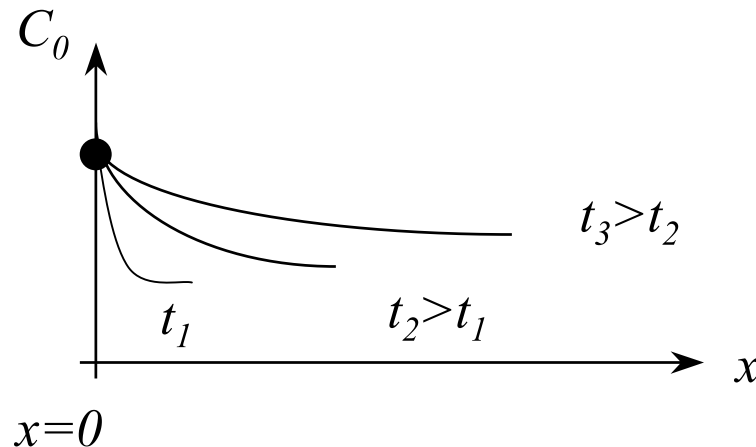
Diffusion under constant surface concentration

$$C(x,t) = C_0 \cdot \left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2} dy \right]$$

$$= C_0 \cdot erfc\left(\frac{x}{2\sqrt{Dt}} \right)$$

$2\sqrt{Dt}$ = Characteristic distance for diffusion.

$C_0 \equiv$ Surface Concentration (solid solubility limit)



Properties of Error Function erf(z) and Complementary Error Function erfc(z)

$$\mathbf{erf\,(z)} = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2}\, dy \qquad \mathbf{erfc\,(z) \equiv 1 - erf\,(z)}$$

$$\mathrm{erf}\,(0) = 0 \qquad \mathrm{erf}(\infty) = 1 \qquad \mathrm{erf}(-\infty) = -1$$

$$\mathrm{erf}\,(z) \approx \frac{2}{\sqrt{\pi}} z \quad \text{for } z \ll 1 \qquad \mathrm{erfc}\,(z) \approx \frac{1}{\sqrt{\pi}} \frac{e^{-z^2}}{z} \quad \text{for } z \gg 1$$

$$\frac{d\,\mathrm{erf}(z)}{dz} = -\frac{d\,\mathrm{erfc}(z)}{dz} = \frac{2}{\sqrt{\pi}} e^{-z^2}$$

$$\frac{d^2\,\mathrm{erf}(z)}{dz^2} = -\frac{4}{\sqrt{\pi}} z\, e^{-z^2}$$

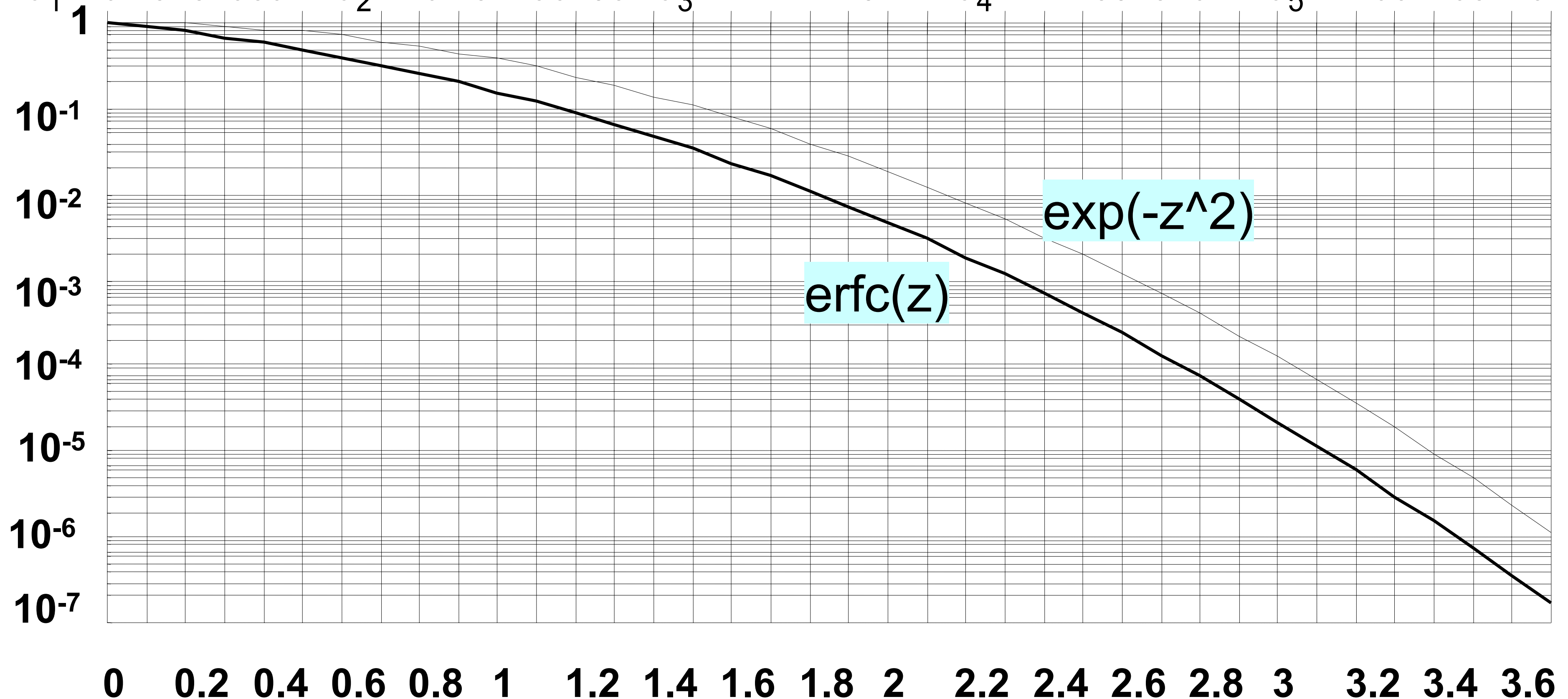
$$\int_0^z \mathrm{erfc}(y)dy = z\,\mathrm{erfc}(z) + \frac{1}{\sqrt{\pi}}(1-e^{-z^2}) \qquad \int_0^\infty \mathrm{erfc}(z)dz = \frac{1}{\sqrt{\pi}}$$

Practical Approximations of erf and erfc

The value of erf(z) can be found in mathematical tables, as build-in functions in calculators and spread sheets. If you have a programmable calculator, this approximation is accurate to 1 part in 10^7: $\text{erf}(z) = 1 - (a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5)\, e^{-z^2}$

where $T = \dfrac{1}{1+P z}$ and $P = 0.3275911$

$a_1 = 0.254829592$ $a_2 = -0.284496736$ $a_3 = 1.421413741$ $a_4 = -1.453152027$ $a_5 = 1.061405429$



[1] Predeposition dose

$$Q(t) = \int_0^{\infty} C(x,t)\,dx$$

$$= \frac{C_0 \cdot 2\sqrt{Dt}}{\sqrt{\pi}} \quad \propto \sqrt{t}$$

[2] Conc. gradient

$$\frac{\partial C}{\partial x} = -\frac{Co}{\sqrt{\pi}\sqrt{Dt}}\, e^{-x^2/4Dt}$$

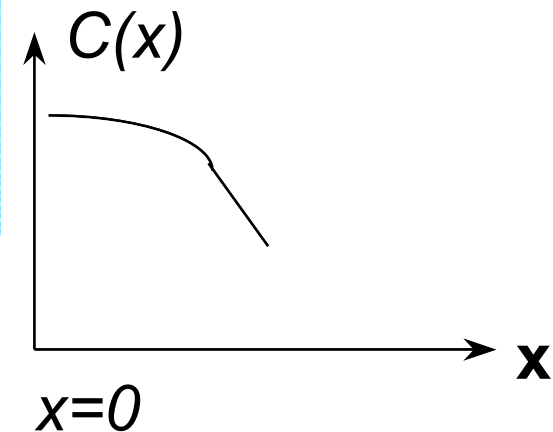
B. Drive-in Profile

- *Boundary Conditions* :

$$C(x=\infty, t) = 0$$

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = 0$$

Physical meaning of ∂C/∂t =0:
No diffusion flux in/out of the Si surface. Therefore, dopant dose is conserved



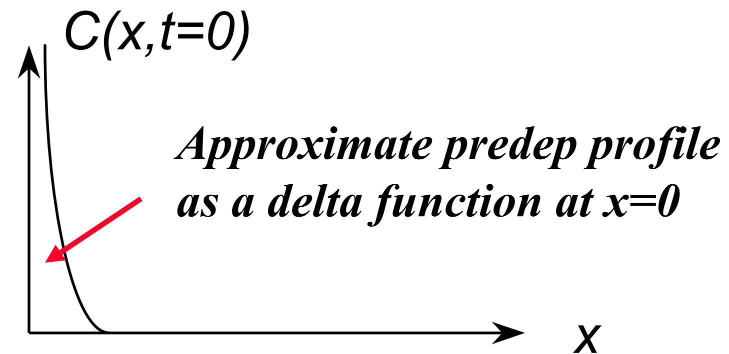
- *Initial Conditions* :

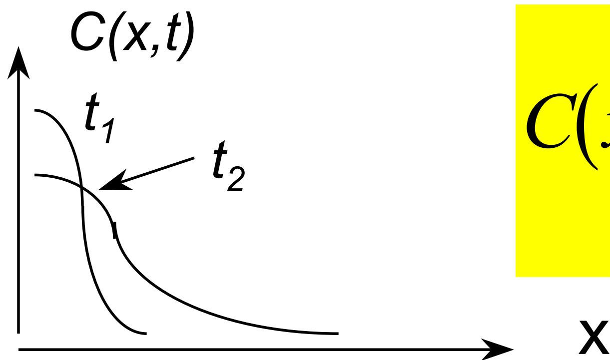
$$C(x, t=0) = Co \cdot erfc\left[\frac{x}{2\sqrt{(Dt)}}\right]$$

Predep's (Dt)

Solution of Drive-in Profile with **Shallow** Predeposition Approximation:

$$Q = \frac{C_0 \cdot 2\sqrt{(Dt)}_{predep}}{\sqrt{\pi}}$$



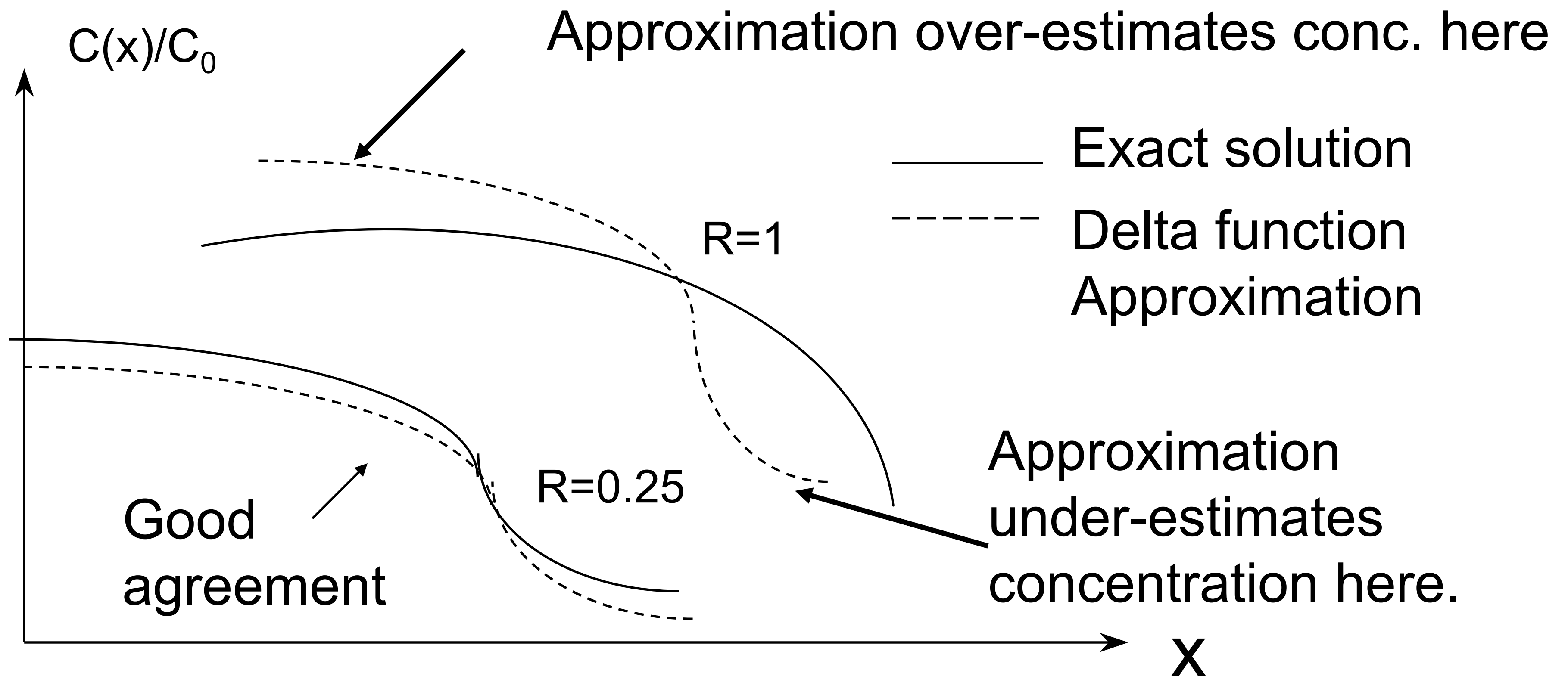


$$C(x,t) = \frac{Q}{\sqrt{\pi (Dt)_{drive-in}}} e^{-x^2 / 4(Dt)_{drive-in}}$$

How good is the δ(x) approximation ?

For reference only

$$Let \quad R \equiv \frac{\sqrt{Dt}_{predep}}{\sqrt{Dt}_{drive-in}}$$



Summary of Predeposition + Drive-in

$D_1 =$ Diffusivity at Predeposition temperature

$t_1 =$ Predeposition time

$D_2 =$ Diffusivity at Drive-in temperature

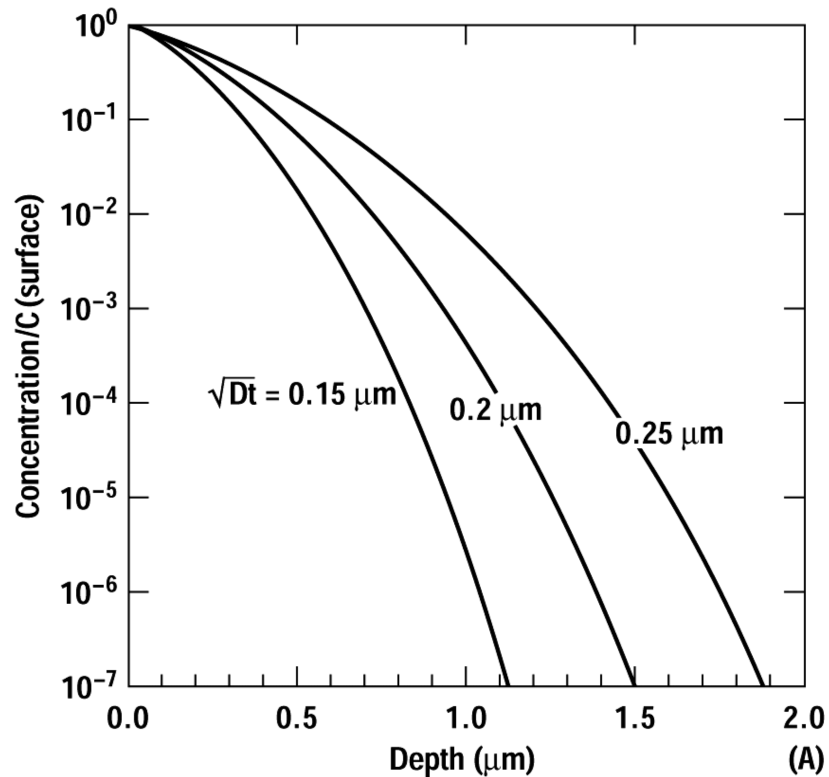
$t_2 =$ Drive-in time

$$C(x) = \left(\frac{2C_0}{\pi}\right)\left(\frac{D_1 t_1}{D_2 t_2}\right)^{1/2} e^{-x^2 / 4 D_2 t_2}$$

*This will be the overall diffusion profile after a “shallow” predeposition diffusion step, followed by a drive-in diffusion step.

Semilog Plots of normalized Concentration versus depth

Predeposition



Drive-in

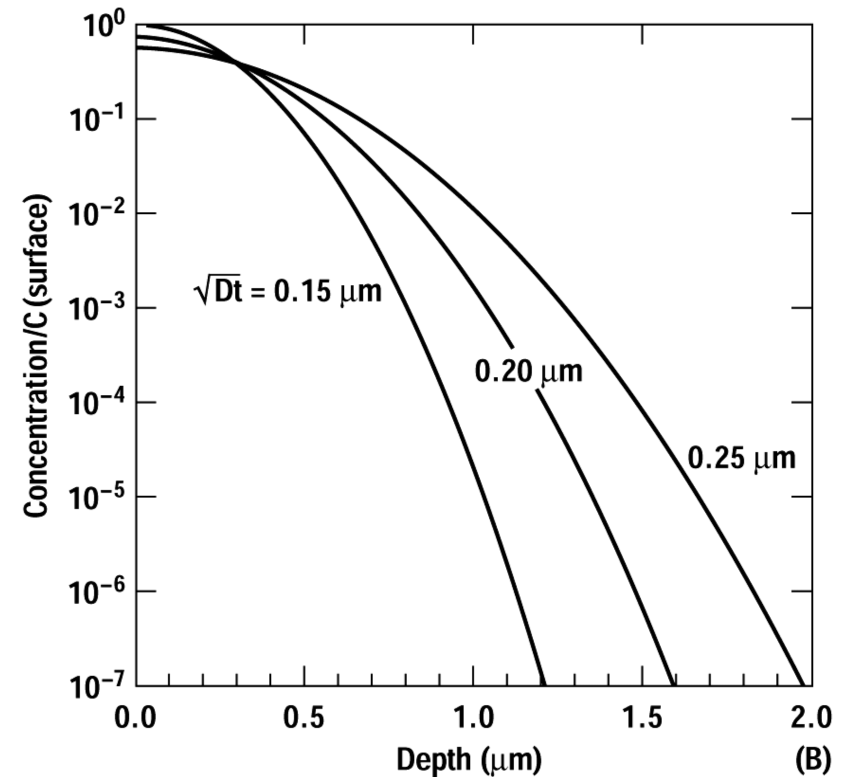
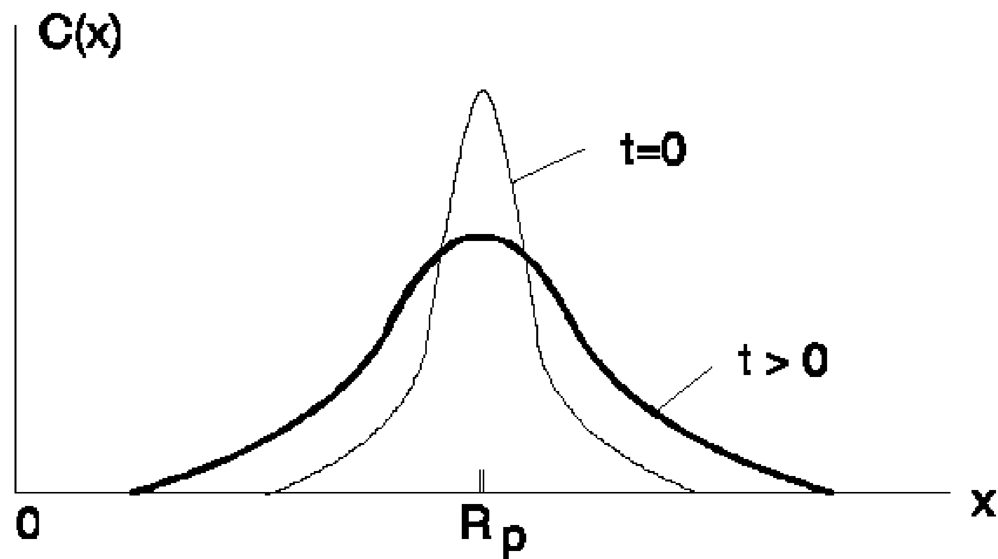


Figure 3.7 Concentration as a function of depth for (A) predeposition and (B) drive in diffusions for several values of the characteristic diffusion length.

Diffusion of Gaussian Implantation Profile



$$C(x, t) = \frac{\phi}{\sqrt{2\pi}\,(\Delta R_p^2 + 2Dt)^{1/2}} \cdot e^{-\frac{(x - R_p)^2}{2\,(\Delta R_p^2 + 2Dt)}}$$

Note: ϕ is the implantation dose

Diffusion of Gaussian Implantation Profile (arbitrary Rp)

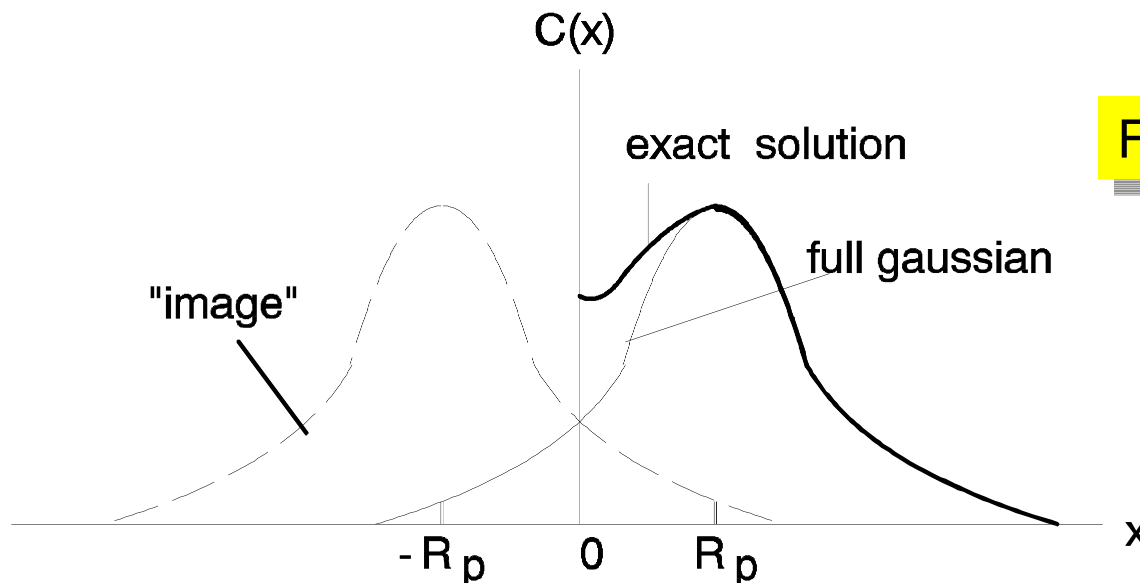
The exact solutions with $\frac{\partial C}{\partial x} = 0$ at x = 0 (.i.e. no dopant loss through surface) can be constructed by adding another full gaussian placed at $-R_p$ [Method of Images].

$$C(x, t) = \frac{\phi}{\sqrt{2\pi}\,(\Delta R_p^2 + 2Dt)^{1/2}} \cdot \left[e^{-\frac{(x - R_p)^2}{2(\Delta R_p^2 + 2Dt)}} + e^{-\frac{(x + R_p)^2}{2(\Delta R_p^2 + 2Dt)}} \right]$$

We can see that in the limit $(Dt)^{1/2} >> R_p$ and ΔR_p ,

$$C(x,t) \rightarrow \frac{\phi e^{-x^2/4Dt}}{(\pi D t)^{1/2}}$$

(the half-gaussian drive-in solution)



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The Thermal Budget

Dopants will redistribute when subjected to various thermal cycles of IC processing steps. If the diffusion constants at each step are independent of dopant concentration, the diffusion equation can be written as:

$$\frac{\partial C}{\partial t} = D(t) \frac{\partial^2 C}{\partial x^2}$$

Let $\beta(t) \equiv \int_0^t D(t')dt'$

$$\therefore D(t) = \frac{\partial \beta}{\partial t}$$

Using $\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \beta} \bullet \frac{\partial \beta}{\partial t}$

The diffusion equation becomes: $\frac{\partial C}{\partial \beta} \bullet \frac{\partial \beta}{\partial t} = \frac{\partial \beta}{\partial t} \bullet \frac{\partial^2 C}{\partial x^2}$ or $\frac{\partial C}{\partial \beta} = \frac{\partial^2 C}{\partial x^2}$

When we compare that to a standard diffusion equation with D being time-independent: $\frac{\partial C}{\partial (Dt)} = \frac{\partial^2 C}{\partial x^2}$, we can see that replacing the (Dt) product in the standard solution by β will also satisfy the time-dependent D diffusion equation.

Example

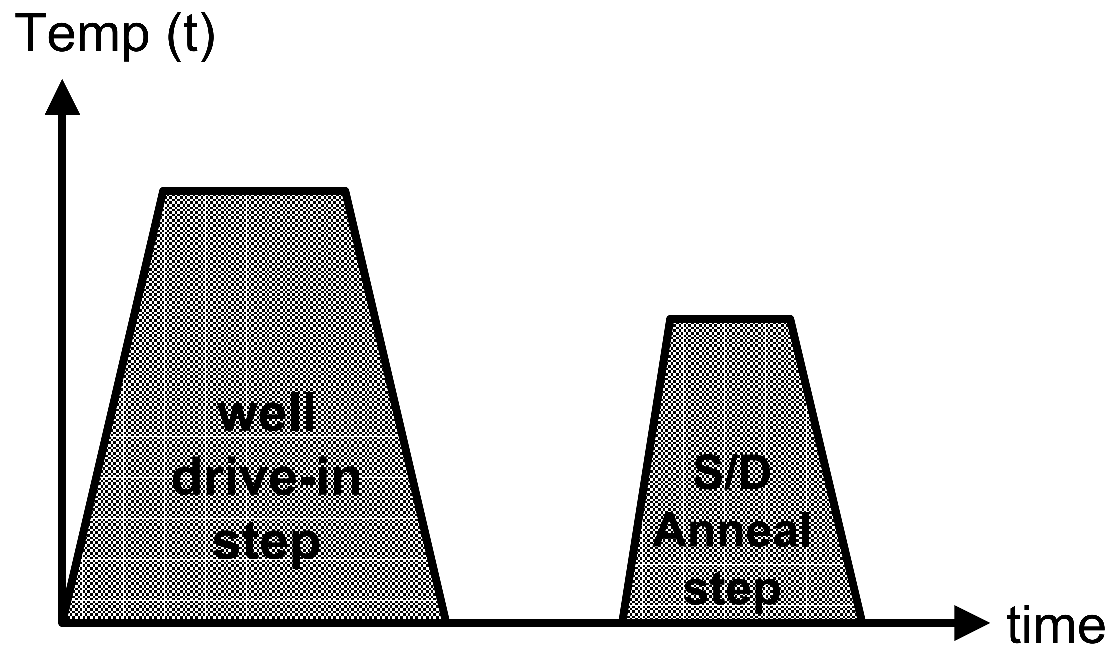
Consider a series of high-temperature processing cycles at {temperature T_1, time duration t_1} ,{ temperature T_2, time duration t_2 }, etc. The corresponding diffusion constants will be D_1, D_2,... . Then,

$\beta = D_1 t_1 + D_2 t_2 + ... = (Dt)_{effective}$

** The sum of Dt products is sometimes referred to as the "thermal budget" of the process. For small dimension IC devices, dopant redistribution has to be minimized and we need low thermal budget processes.

Thermal Budget

$$(Dt)_{effective} = \sum_{\text{step } i} (Dt)_i$$



Example

Dt_{total} of :

Well drive-in

and

S/D annealing

For a complete process flow, only those steps with high Dt values are important

Irvin's Curves

p-type erfc
n-type erfc
p-type half-gaussian
n-type half-gaussian

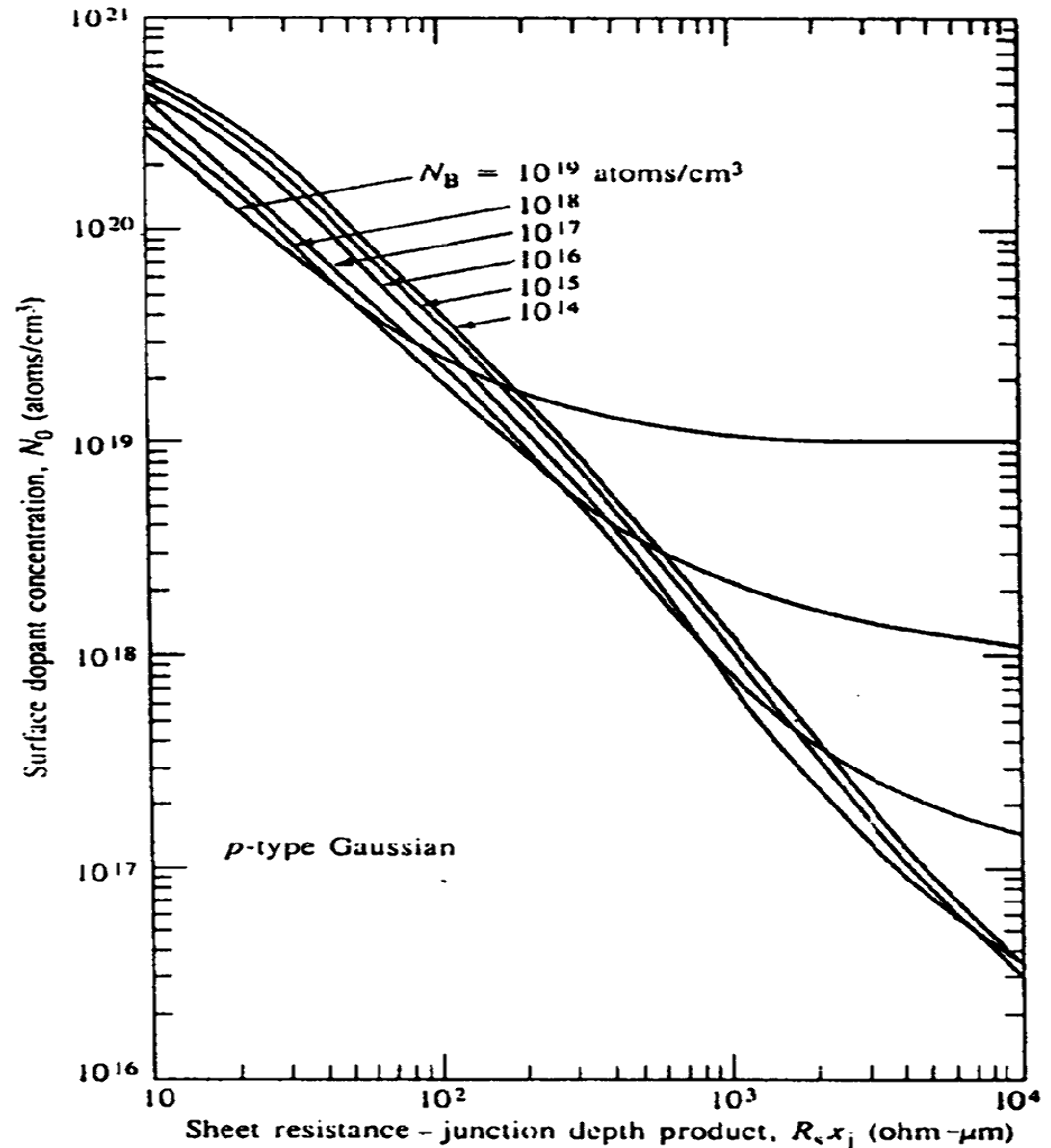
Explicit relationship between:

N_o (surface concentration) ,

x_j (junction depth),

N_B (background concentration)

R_S (sheet resistance),



Once any three parameters are known, the fourth one can be determined.

Motivation to generate the Irvin's Curves

Both N_B(4-point-probe), R_S (4-point probe) and x_j (junction staining) can be conveniently measured experimentally but not N_o (requires secondary ion mass spectrometry). However, these four parameters are related.

Approach

1) The dopant profile (erfc or half-gaussian) can be uniquely determined if one knows the concentration values at ***two*** depth positions.

2) We will use the concentration values N_o at x=0 and N_B at $x=x_j$ to determine the profile C(x). (i.e., we can determine the Dt value)

3) Once the profile C(x) is known, the sheet resistance R_S can be integrated numerically from:

$$Rs = \frac{1}{\int_0^{x_j} q \cdot \mu(x)[C(x) - N_B]dx}$$

4) Irvin's Curves are plots of N_o versus ($R_s \bullet x_j$) for various N_B.

Illustrating the relationship of N_o, N_B, x_j, and R_S