# Diffusion Mechanisms

- **probability of movement**
  - $\nu \cong 4\,\nu_0\,e^{-E/kT}$, $\nu_o$ **~ $10^{13}$ - $10^{14}$ sec$^{-1}$**

- **interstitial diffusers**
  - $E_{move}$ **~ 0.6 - 1.2 eV**
    - **T = 300K: $\nu$ ~ 1 jump per minute**
    - **T = 1300K: $\nu$ ~ $10^9$ jumps per sec**

- **substitutional diffusers**
  - $E_{move}$ **~ 3 - 4 eV**
    - **T = 300K: $\nu$ ~ 1 jump per $10^{30}$ - $10^{40}$ years!**
    - **T = 1300K: $\nu$ ~ few jumps per sec**



substitutional impurity

vacancy

interstitial impurity

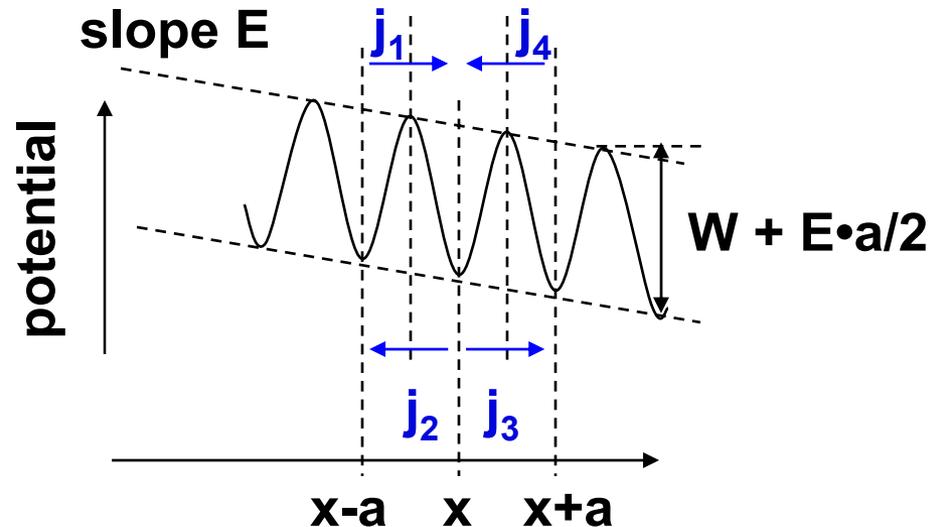interstitialcy mechanism
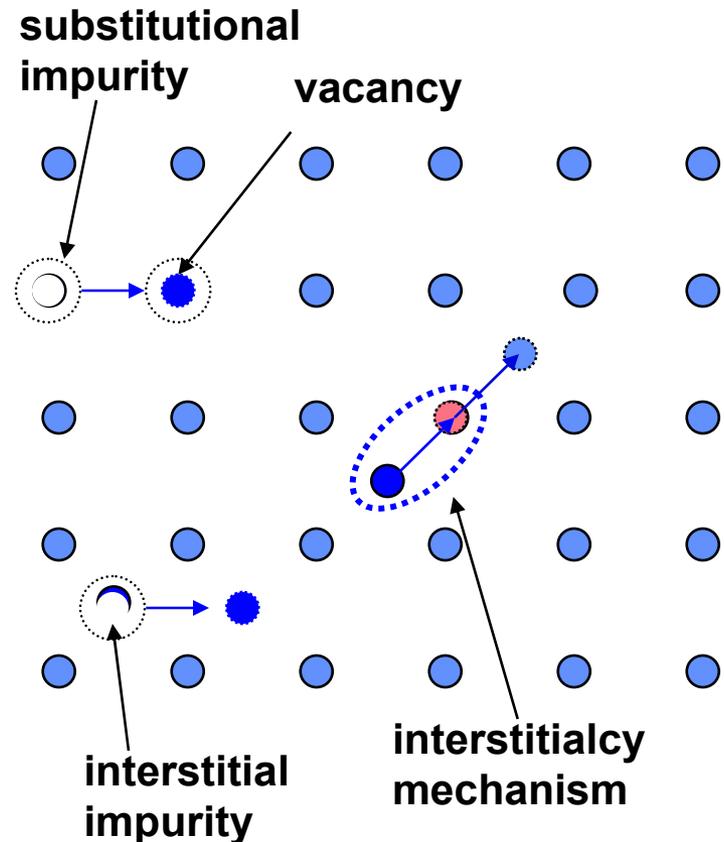
# Fick's First Law and "field assisted" diffusion

- **impurity sees a periodic (crystal) potential**
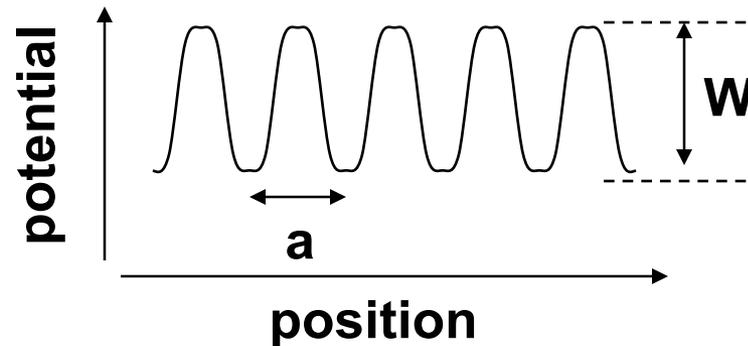


- **with applied field**

- **goal: find the flux passing through plane at position x**

# Probability of jumping and flux

- **barrier for jumps to the left is higher than to the right**
  - **jump-to-the-left barrier:  W + (E • a/2)**
  - **jump-to-the-right barrier:  W - (E • a/2)**
- **flux is      j  =  (# of ions / area) •**
  **(prob. of surmounting barrier) •**
  **(frequency of jump attempts)**

  **=  (concentration • "thickness") •**
  **exp[- barrier / kT]   •   $\nu_o$**

  **=  ( $N_{imp}$ • a ) • exp[- barrier / kT] • $\nu_o$**

- **$j_1$ =   $\nu_o$ • a • N(x-a) • exp[ - q(W - E•a/2) / kT]**
- **$j_2$ =   $\nu_o$ • a • N(x) • exp[ - q(W + E•a/2) / kT]**
- **$j_3$ =   $\nu_o$ • a • N(x) • exp[ - q(W - E•a/2) / kT]**
- **$j_4$ =   $\nu_o$ • a • N(x+a) • exp[ - q(W + E•a/2) / kT]**

# Flux through plane at location x



- **"average" "net flux" used for j(x)**
  - **flux crossing plane at (x - a/2)**
    **= ($j_1$ - $j_2$)**
  - **flux crossing plane at (x + a/2)**
    **= ($j_3$ - $j_4$)**
  - **j(x) ≈ [ ($j_1$ - $j_2$) + ($j_3$ - $j_4$) ] / 2**
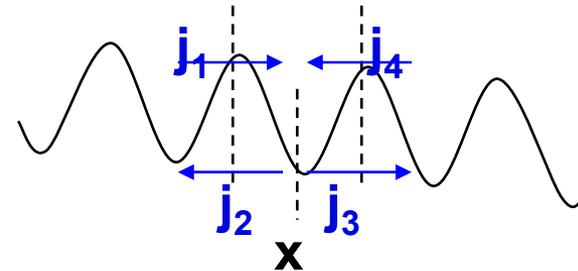
$$j_1 = \nu_o \cdot a \cdot N(x-a) \cdot \exp[ - q(W - E\cdot a/2) / kT]$$
$$j_2 = \nu_o \cdot a \cdot N(x) \cdot \exp[ - q(W + E\cdot a/2) / kT]$$
$$j_3 = \nu_o \cdot a \cdot N(x) \cdot \exp[ - q(W - E\cdot a/2) / kT]$$
$$j_4 = \nu_o \cdot a \cdot N(x+a) \cdot \exp[ - q(W + E\cdot a/2) / kT]$$

- **what about N(x±a)?**
  - **use one term Taylor series approximation:  N(x±a) ≈ N(x) ± a• ∂N/∂x**

- **combining terms gives**

$$j(x) = \frac{\nu_o}{2} \cdot e^{-\frac{q}{kT}W} \cdot \left[ 2aN(x) \cdot \left( e^{\frac{q}{2kT}aE} - e^{-\frac{q}{2kT}aE} \right) \right.$$

$$\left. - a^2 \frac{\partial N}{\partial x}\bigg|_x \cdot \left( e^{\frac{q}{2kT}aE} + e^{-\frac{q}{2kT}aE} \right) \right]$$

# Flux result

- **rearranging terms gives**

$$j(x) = 2\,\nu_o \cdot a \cdot e^{-\frac{q}{kT}W} \cdot N(x) \cdot \sinh\left(\frac{q}{2kT}\,aE\right)$$

$$-\,\nu_o \cdot a^2 \cdot e^{-\frac{q}{kT}W} \cdot \frac{\partial N}{\partial x} \cdot \cosh\left(\frac{q}{2kT}\,aE\right)$$

  - **for "small" fields**
    **(i.e., E << kT/qa ≈ MV/cm @ 1000˚C)**
    - **cosh (q a E / 2kT) ≈ 1**
    - **sinh (q a E / 2kT) ≈ q a E / 2kT**

- **then**

$$j(x) = \left(\frac{\nu_o \cdot a^2}{kT/q} \cdot e^{-\frac{q}{kT}W}\right) \cdot N(x) \cdot E - \left(\nu_o \cdot a^2 \cdot e^{-\frac{q}{kT}W}\right) \cdot \frac{\partial N}{\partial x}$$

$$= \mu \cdot N(x) \cdot E - D \cdot \frac{\partial N}{\partial x}$$

  - **where**

$$D \stackrel{def}{=} \nu_o \cdot a^2 \cdot e^{-\frac{q}{kT}W} \left(\frac{cm^2}{sec}\right) \qquad \mu \stackrel{def}{=} \frac{\nu_o \cdot a^2}{kT/q} \cdot e^{-\frac{q}{kT}W} \left(\frac{cm^2}{volt \cdot sec}\right)$$

# Drift-Diffusion Equation

- **we have found the basic transport equation**

$$j(x) = \underbrace{\mu \cdot N(x) \cdot E}_{\text{"drift"}} - \underbrace{D \cdot \frac{\partial N}{\partial x}}_{\text{"diffusion"}}$$

  - **where**
    - $\mu$ **is the mobility**
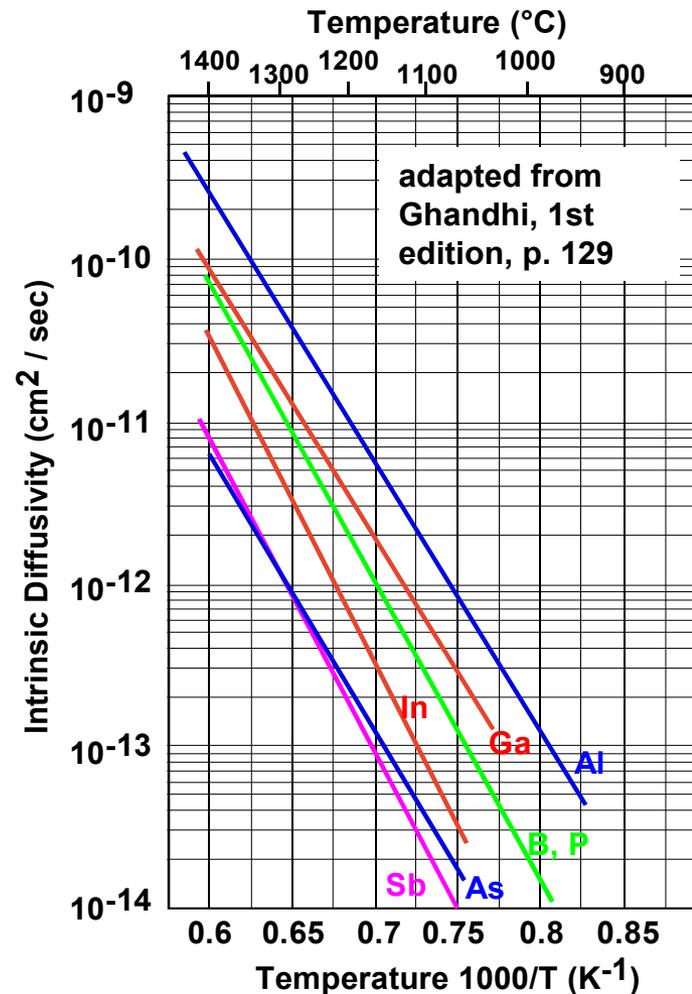    - **D is the diffusivity**

- **note that**

$$\frac{D}{\mu} = \frac{\nu_o \cdot a^2 \cdot e^{-\frac{q}{kT}W}}{\frac{\nu_o \cdot a^2}{kT/q} \cdot e^{-\frac{q}{kT}W}} = \frac{kT}{q}$$

  - **this is called Einstein's relationship**

# Magnitudes of diffusivity

- **substitutional diffusers in Si**
    - column III: Al, B, Ga, In
    - column V: Sb, As, P



adapted from Ghandhi, 1st edition, p. 129

# Is the diffusivity independent of impurity concentration?

- **before we can use the diffusion equation we need to know if D depends on N**
    - **what about internally generated fields?**



  With labels: $E_{CBE}$, $E_i$, $E_{fermi}$, $E_{VBE}$, and axis $x$.
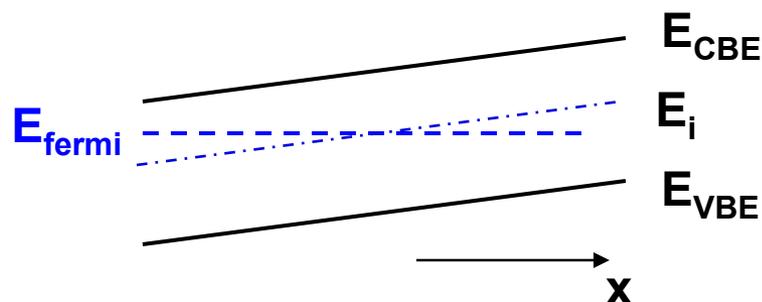
    - **if the fermi level is not shown, can't tell the difference between concentration gradient and electric field (F)**
    - **basic relationships:**
        - **internal electric field**

$$F_{int} = \frac{1}{q} \frac{\partial E_i}{\partial x} \quad (1)$$

        - **carrier concentration**

$$n = n_i \, e^{(E_f - E_i)/kT} \quad (2)$$

# Impact of internal field on diffusion

- **consider ∂n/∂x from eq. 2**
$$\frac{\partial n}{\partial x} = \frac{\partial}{\partial x}\left[ n_i e^{(E_f - E_i)/kT} \right] = \underbrace{n_i e^{(E_f - E_i)/kT}}_{n} \cdot \underbrace{\frac{\partial}{\partial x}\left[ (E_f - E_i)/kT \right]}_{-\frac{\partial E_i}{\partial x}\Big/ kT}$$

  - **or**
$$\frac{\partial n}{\partial x} = -\frac{n}{kT} \cdot \underbrace{\frac{\partial E_i}{\partial x}}_{qF_{\text{int}}} = -\frac{nq}{kT} \cdot F_{\text{int}}$$

  - **so**
$$F_{\text{int}} = -\frac{kT}{q} \cdot \frac{1}{n} \cdot \frac{\partial n}{\partial x}$$

- **now substitute into drift-diffusion equation**
$$j(x) = D \cdot \frac{q}{kT} \cdot N \cdot F_{\text{int}} - D \cdot \frac{\partial N}{\partial x} = -D \cdot \left[ \frac{q}{kT} \cdot N \cdot \left( \frac{kT}{q} \frac{1}{n} \frac{\partial n}{\partial x} \right) + \frac{\partial N}{\partial x} \right]$$

$$j(x) = -D \cdot \left[ \frac{N}{n} \frac{\partial n}{\partial x} + \frac{\partial N}{\partial x} \right] = -D \cdot \left[ \frac{N}{n} \frac{\partial n}{\partial N} + 1 \right] \cdot \frac{\partial N}{\partial x}$$

$$= -D_{eff} \cdot \frac{\partial N}{\partial x}$$

- **where**
$$D_{eff} \overset{\text{definition}}{=} D \cdot \left[ \frac{N}{n} \frac{\partial n}{\partial N} + 1 \right]$$

# Impact of internal field on diffusion

- **how big can $D_{eff}$ be?**

$$D_{eff} \overset{\text{definition}}{=} D \cdot \left[ \frac{N}{n} \frac{\partial n}{\partial N} + 1 \right]$$

   – **recall "law of mass action"**    $p \cdot n = (n_i)^2$

   – **space charge neutrality**    $n^- = p^+ + N_D^+$

   – **yields**    $n = \frac{1}{2} \left\{ N_D + \sqrt{(N_D)^2 + 4(n_i)^2} \right\}$

   – **so**    $$\frac{\partial n}{\partial N} = \frac{1}{2} \left\{ 1 + \frac{1}{\sqrt{1 + 4(n_i/N)^2}} \right\}$$

# Concentration dependent diffusivity

$$D_{eff} \overset{definition}{=} D \cdot \left[ \frac{N}{n} \frac{\partial n}{\partial N} + 1 \right]$$

$$\frac{\partial n}{\partial N} = \tfrac{1}{2} \left\{ 1 + \frac{1}{\sqrt{1 + 4(n_i/N)^2}} \right\}$$
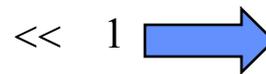
- **intrinsic case**
  - **N << $n_i$ , n ≈ $n_i$**      $\frac{n_i}{N} \gg 1$      $\frac{N}{n} \ll 1$

$$\left( \sqrt{1 + \underbrace{4(n_i/N)^2}_{\gg 1}} \right)^{-1} \ll 1 \implies \frac{\partial n}{\partial N} = \tfrac{1}{2}\{1 + (\ll 1)\} \approx \tfrac{1}{2}$$

$$D_{eff} = D \cdot \left[ \underbrace{\frac{N}{n}}_{\ll 1} \cdot \underbrace{\frac{\partial n}{\partial N}}_{\approx 1/2} + 1 \right] \approx D$$

- **for intrinsic case $D_{eff}$ is just D, independent of impurity concentration!**
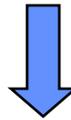  - **there is NO conc. dependence here!**

# Concentration dependent diffusivity

$$\frac{\partial n}{\partial N} = \tfrac{1}{2}\left\{1 + \frac{1}{\sqrt{1 + 4(n_i/N)^2}}\right\}$$

- **extrinsic case**
  - **N >> $n_i$, n ≈ $N_D$**   $\dfrac{n_i}{N} \ll 1$   $\dfrac{N}{n} \approx 1$

$$\frac{1}{\sqrt{1 + \underbrace{4(n_i/N)^2}_{\ll 1}}} \approx 1 \qquad\Longrightarrow\qquad \frac{\partial n}{\partial N} = \tfrac{1}{2}\{1 + (\approx 1)\} \approx 1$$

$$D_{eff} = D \cdot \left[\underbrace{\frac{N}{n}}_{\approx 1} \cdot \underbrace{\frac{\partial n}{\partial N}}_{\approx 1} + 1\right] \approx 2 \cdot D$$

- **for extrinsic case $D_{eff}$ is 2*D**
  - **there is some conc. dependence as you change from N << $n_i$ to N >> $n_i$**

# Concentration dependent diffusivity

- **expect only for "high" impurity concentration**
  - **high compared to <u>intrinsic carrier concentration at the diffusion temperature</u>!**

  - **intrinsic diffusion: $N_{imp} \ll n_i$  (n, p ≈ $n_i$)**
    - **D independent of $N_{imp}$**
  - **extrinsic diffusion: $N_{imp} \gg n_i$  (n or p ≈ $N_{imp}$)**
    - **D may depend on $N_{imp}$**



Temperature (°C) / Intrinsic carrier concentration (#/cm³) vs Temperature (K)
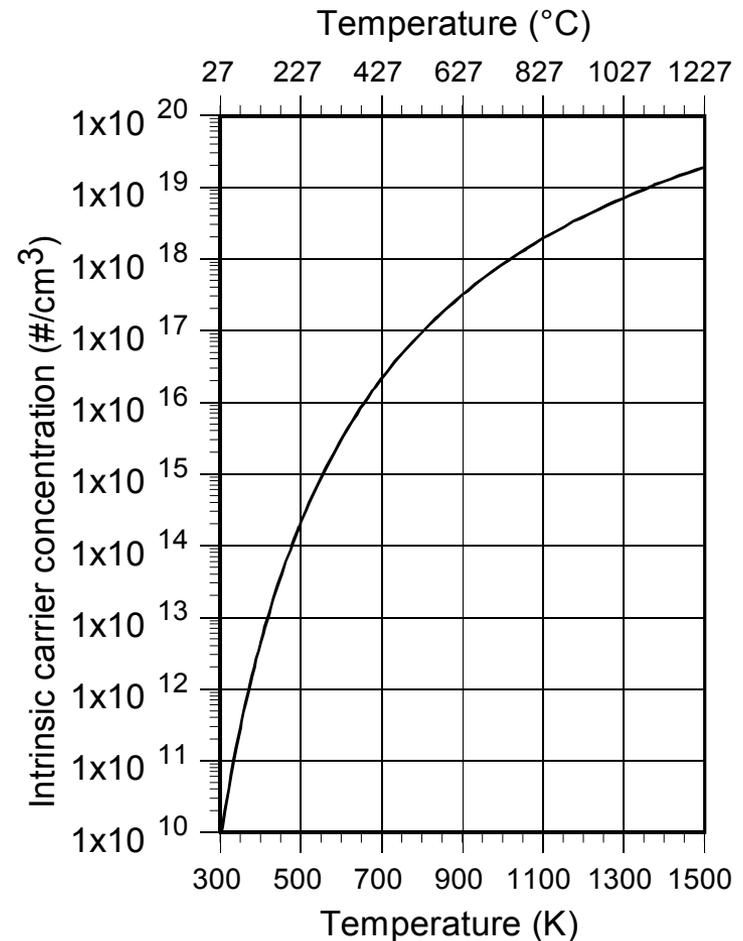
# Interactions with charged defects

- **problem: observed $D_{eff}$ for N > $n_i$ is more than $2D_{intrinsic}$**
- **consider interactions between charged impurities and charged defects**
  - **assume defects of interest are vacancies**
  - **assume each interaction contributes linearly to the total diffusivity**
  - **assume size of contribution is proportional to relative concentration of the particular defect charge state**

$$D \;=\; D_i^0 \cdot \frac{\left[V^0\right]}{\left[V^0\right]_i} \;+\; D_i^{1+} \cdot \frac{\left[V^{1+}\right]}{\left[V^{1+}\right]_i} \;+\; D_i^{2+} \cdot \frac{\left[V^{2+}\right]}{\left[V^{2+}\right]_i} \;+\; \cdots$$

$$+\; D_i^{1-} \cdot \frac{\left[V^{1-}\right]}{\left[V^{1-}\right]_i} \;+\; D_i^{2-} \cdot \frac{\left[V^{2-}\right]}{\left[V^{2-}\right]_i} \;+\; \cdots$$

  - **superscript indicates charge state**
  - **subscript "i" indicates intrinsic value**
  - **[ ] indicates concentration**

# Does [V$^{r\pm}$] / [V$^{r\pm}$]$_i$ depend on anything?

– **interactions are electrostatic**
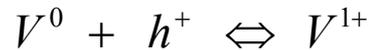
– **BUT neutral state cannot interact via electric field**

$$\left[V^0\right] = \left[V^0\right]_i \quad \Rightarrow \quad \frac{\left[V^0\right]}{\left[V^0\right]_i} = 1$$

• **neutral term never changes!!**

# First charged term $\dfrac{\left[V^{1+}\right]}{\left[V^{1+}\right]_i}$

- **charged defect formed from neutral defect in equilibrium reaction**

$$V^0 \;+\; h^+ \;\Leftrightarrow\; V^{1+}$$

- **recall that for a chemical reaction of the form**

$$a \cdot A \;+\; b \cdot B \;\Leftrightarrow\; c \cdot C$$

- **the concentrations are related to the equilibrium constant k by Rault's Law**

$$\frac{\left[C\right]^c}{\left[A\right]^a \cdot \left[B\right]^b} \;=\; k$$

- **here a = b = c = 1, [A] = [V$^0$], [B] = [h] = p, [C] = [V$^{1+}$], so**

$$\overbrace{\frac{\left[V^{1+}\right]_i}{\underbrace{p}_{p\,=\,n_i} \cdot \left[V^0\right]_i}}^{intrinsic} \;=\; k \qquad \overbrace{\frac{\left[V^{1+}\right]}{p \cdot \underbrace{\left[V^0\right]}_{=\left[V^0\right]_i}}}^{extrinsic} \;=\; k \quad\Rightarrow\quad \frac{\left[V^{1+}\right]_i}{n_i \cdot \left[V^0\right]_i} \;=\; \frac{\left[V^{1+}\right]}{p \cdot \left[V^0\right]_i} \quad\Rightarrow\quad \frac{\left[V^{1+}\right]}{\left[V^{1+}\right]_i} \;=\; \frac{p}{n_i}$$

**these are exactly the same  k!!!**

# General charged term
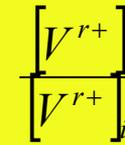
$$\dfrac{\left[V^{r+}\right]}{\left[V^{r+}\right]_i}$$

- **charged defect formed from neutral defect in equilibrium reaction**

$$V^0 + r \cdot h^+ \Leftrightarrow V^{r+}$$

- **so**
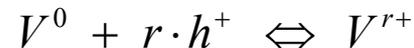
$$\overbrace{\dfrac{\left[V^{r+}\right]_i}{\left(n_i\right)^r \cdot \left[V^0\right]_i}}^{\text{"intrinsic"}} = k = \overbrace{\dfrac{\left[V^{r+}\right]}{\left(p\right)^r \cdot \underbrace{\left[V^0\right]}_{=\left[V^0\right]_i}}}^{\text{"extrinsic"}} \implies \dfrac{\left[V^{r+}\right]}{\left[V^{r+}\right]_i} = \left(\dfrac{p}{n_i}\right)^r$$

- **similarly**

$$\overbrace{\dfrac{\left[V^{r-}\right]_i}{\left(n_i\right)^r \cdot \left[V^0\right]_i}}^{\text{"intrinsic"}} = k = \overbrace{\dfrac{\left[V^{r-}\right]}{\left(n\right)^r \cdot \underbrace{\left[V^0\right]}_{=\left[V^0\right]_i}}}^{\text{"extrinsic"}} \implies \dfrac{\left[V^{r-}\right]}{\left[V^{r-}\right]_i} = \left(\dfrac{n}{n_i}\right)^r$$

# Final result for D(N)

- **combining terms gives**

$$D = D_i^0 + D_i^{1+} \cdot \frac{p}{n_i} + D_i^{2+} \cdot \left(\frac{p}{n_i}\right)^2 + \cdots$$

$$+ D_i^{1-} \cdot \frac{n}{n_i} + D_i^{2-} \cdot \left(\frac{n}{n_i}\right)^2 + \cdots$$

  - **for the intrinsic case n, p = $n_i$, so D = constant, independent of $N_{imp}$**

- **if we assume simple extrinsic conditions**
  - **for donors n ≈ $N_D$, p << $n_i$**

$$D = D_i^0 + D_i^{1-} \cdot \frac{N_D}{n_i} + D_i^{2-} \cdot \left(\frac{N_D}{n_i}\right)^2 + \cdots$$

  - **for acceptors p ≈ $N_A$, n << $n_i$**

$$D = D_i^0 + D_i^{1+} \cdot \frac{N_A}{n_i} + D_i^{2+} \cdot \left(\frac{N_A}{n_i}\right)^2 + \cdots$$

- **so we need to know what defect charge states exist, and their associated D's**

# Vacancy states in Si

- **silicon exhibits four vacancy states**
  - $V^{+1}$, $V^0$, $V^{-1}$, $V^{2-}$

CBE ─────────────── $V^{2-}$

─────────────── $V^{1-}$
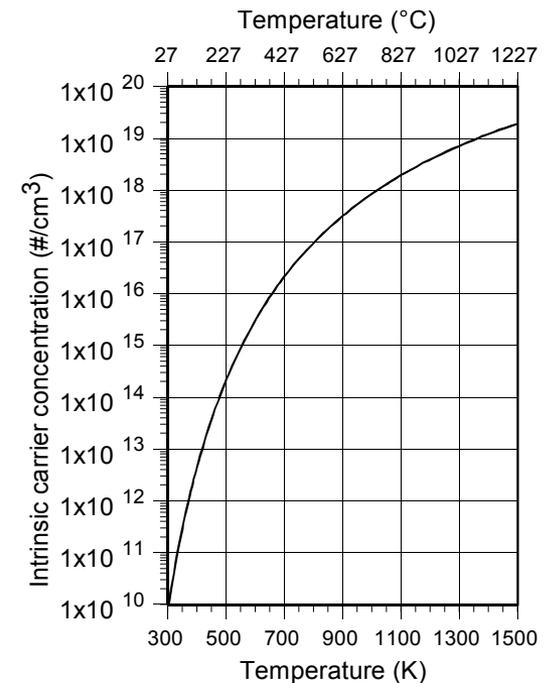
─────────────── $V^{1+}$

VBE ───────────
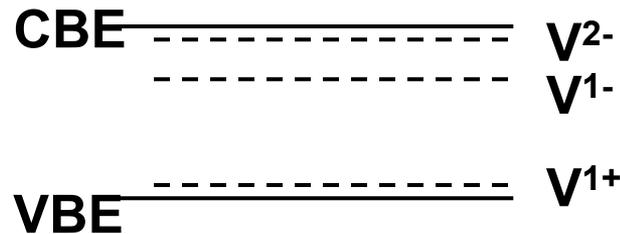
  - **$V^0$ and $V^{+1}$ interactions dominate for p-type dopants**

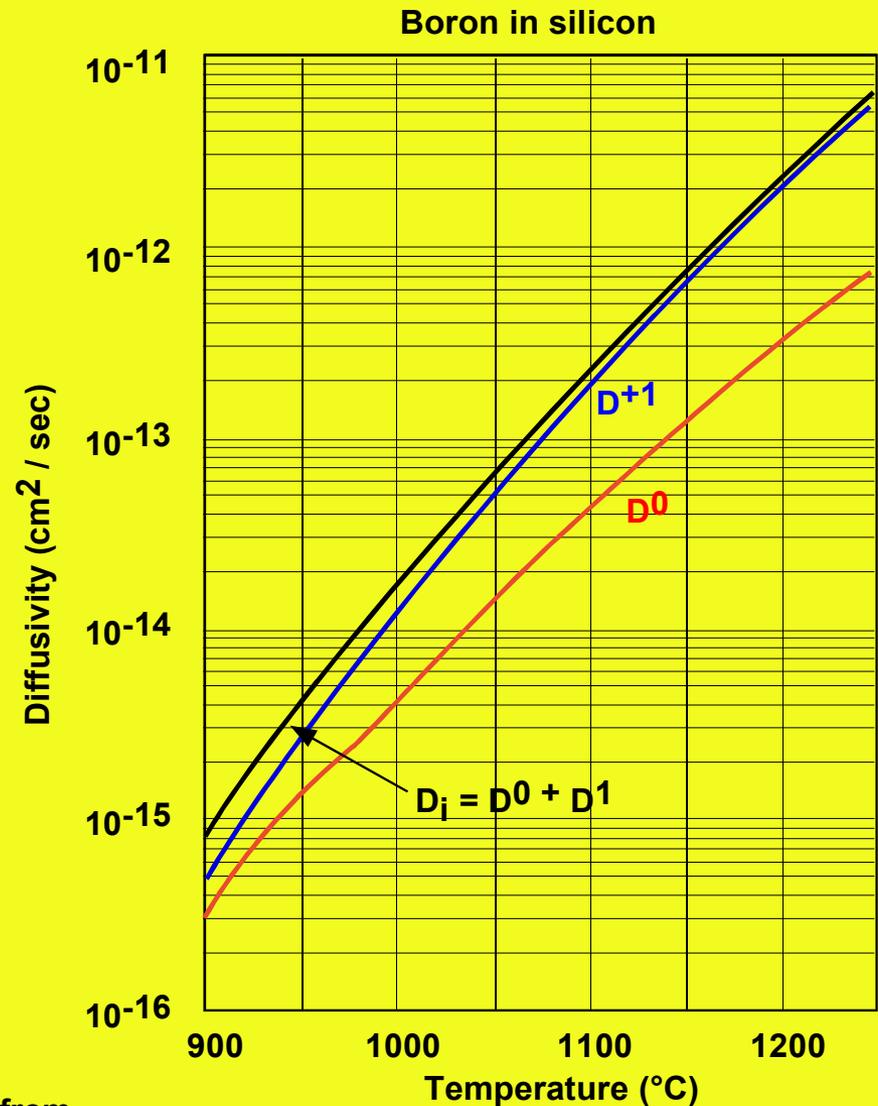$$D_{extrinsic} \approx D_i^0 + D_i^{1+} \cdot \frac{N_A}{n_i}$$

  - **$V^0$, $V^{-1}$, $V^{2-}$ dominate for n-type dopants**

$$D_{extrinsic} \approx D_i^0 + D_i^{1-} \cdot \frac{N_D}{n_i} + D_i^{2-} \cdot \left( \frac{N_D}{n_i} \right)^2$$
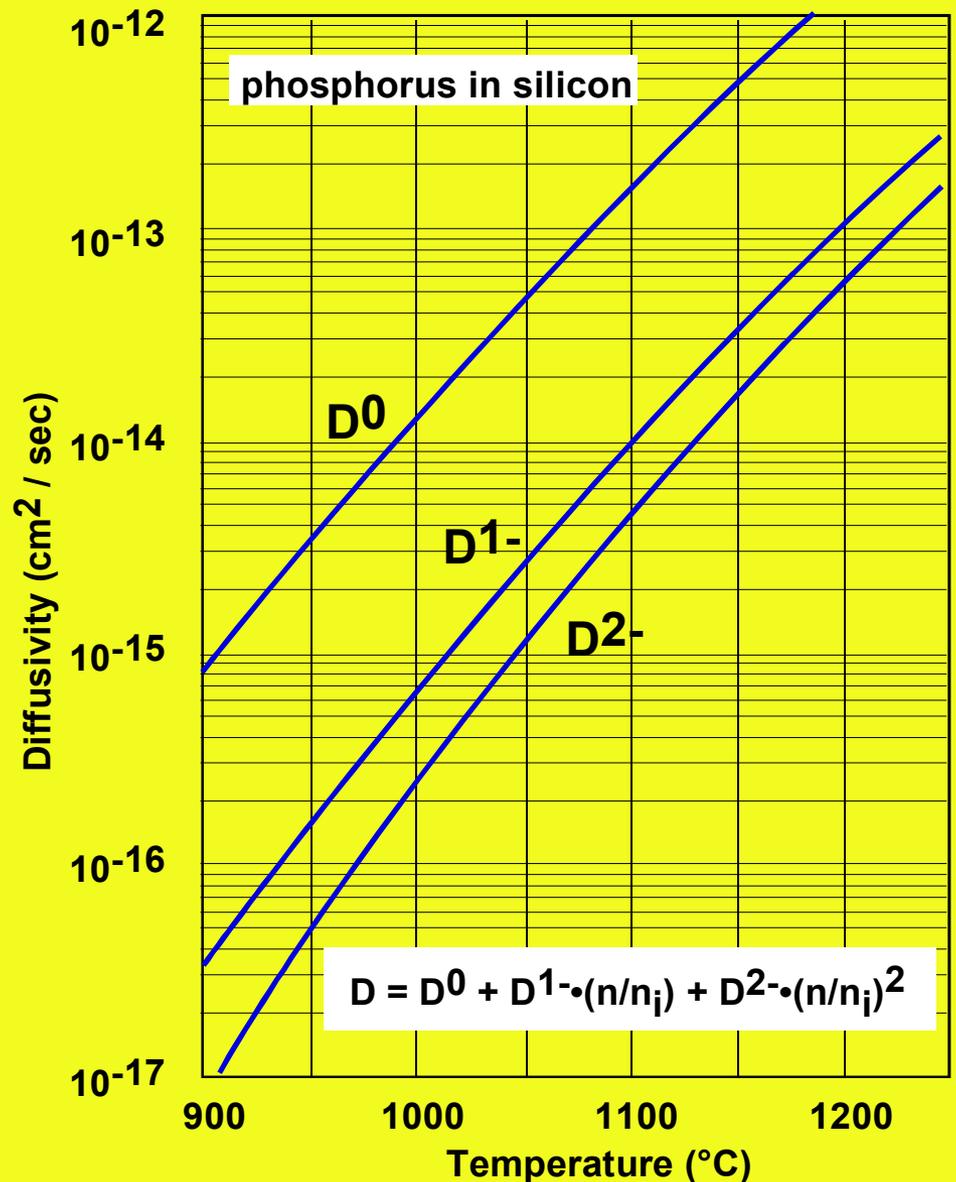
# Boron

- **interactions with neutral and single + defects**
    - $D \approx D^0 + D^{1+} \cdot (p/n_i)$

**Boron in silicon**

Diffusivity ($cm^2$ / sec) vs Temperature (°C)

$D^{+1}$

$D^0$

$D_i = D^0 + D^1$

adapted from
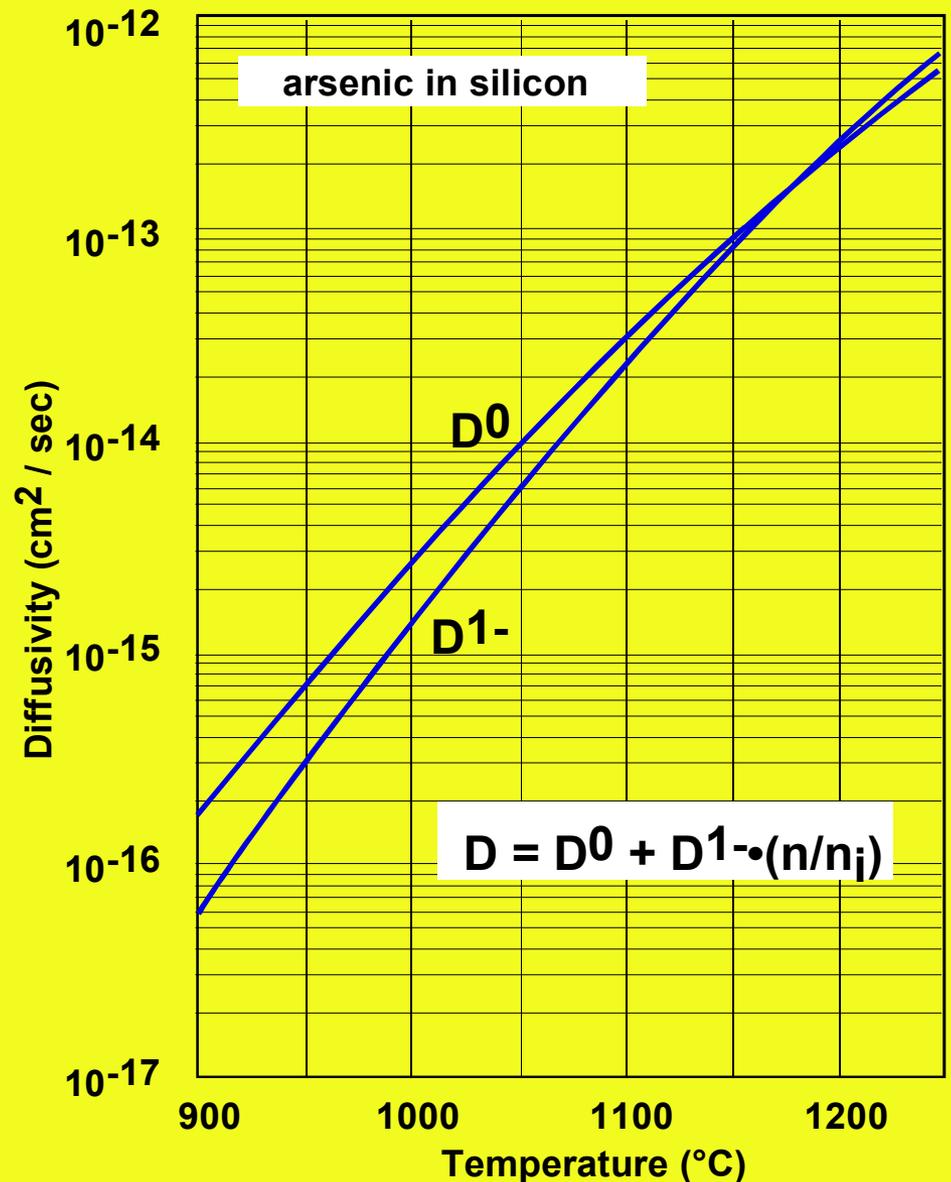Ghandhi, 1st
edition, p. 130

# Phosphorus

- **phosphorus**
  - **interaction with neutral, single - and double - charged defects**
  - $D \approx D^0 + D^{1-} \cdot (n/n_i) + D^{2-} \cdot (n/n_i)^2$

**phosphorus in silicon**

$D^0$

$D^{1-}$

$D^{2-}$

$$D = D^0 + D^{1-} \cdot (n/n_i) + D^{2-} \cdot (n/n_i)^2$$

Diffusivity ($cm^2$ / sec)

$10^{-12}$
$10^{-13}$
$10^{-14}$
$10^{-15}$
$10^{-16}$
$10^{-17}$

900    1000    1100    1200

**Temperature (°C)**

adapted from Ghandhi, 1st edition, p. 131

# Arsenic

- **arsenic**
  - **interaction with neutral and single-charged defects**
  - $D \approx D^0 + D^{1-} \cdot (n/n_i)$



arsenic in silicon

$D^0$

$D^{1-}$

$$D = D^0 + D^{1-} \cdot (n/n_i)$$

Diffusivity (cm$^2$ / sec) vs Temperature (°C)

adapted from Ghandhi, 1st edition, p. 131

# Fick's Second Law: the diffusion equation

- **consider difference between flux entering a small volume and flux leaving that volume**
  - must be related to change in concentration within that volume
  - continuity and conservation of mass gives

$$\underbrace{-\frac{\partial j}{\partial x}}_{\substack{spatial\ rate \\ of\,change \\ of\,flux}} = \underbrace{\frac{\partial N}{\partial t}}_{\substack{time\ rate \\ of\,change \\ of\,particle \\ accumulation}}$$

- **recall Fick's first law (dd with zero field)**

$$j = -D\frac{\partial N}{\partial x}$$

- **so have Fick's second law**

$$\frac{\partial N}{\partial t} = -\frac{\partial}{\partial x}(j) = \frac{\partial}{\partial x}\left(D\frac{\partial N}{\partial x}\right)$$

  - if D is independent of N (and hence of x)

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

# Solutions of the diffusion equation, "constant" D

- **have differential equation in time and space:**  $\dfrac{\partial u}{\partial t} \;=\; D \cdot \dfrac{\partial^2 u}{\partial x^2}$

- **try separation of variables:**  $u(x,\ t) \;=\; X(x) \cdot T(t)$

$$X \cdot \frac{dT}{dt} \;=\; D \cdot T \cdot \left[ \frac{d^2 X}{dx^2} \right]$$

$$\underbrace{\frac{1}{D \cdot T} \cdot \frac{dT}{dt}}_{\text{function of time only}} \;=\; \underbrace{\frac{1}{X} \cdot \left[ \frac{d^2 X}{dx^2} \right]}_{\text{function of dis} \tan \text{ce only}}$$

- **only possible if each side of the equation is equal to a constant (-k$^2$)**
  - **k has units of 1/length**

$$\frac{1}{X} \cdot \frac{d^2 X}{dx^2} \;=\; -k^2 \quad \longrightarrow \quad X \;=\; \left( A \cdot \cos[k \cdot x] \;+\; B \cdot \sin[k \cdot x] \right)$$

$$\frac{1}{T} \cdot \frac{dT}{dt} = -D \cdot k^2 \quad \longrightarrow \quad T \;=\; \exp\left( -D \cdot k^2 \cdot t \right)$$
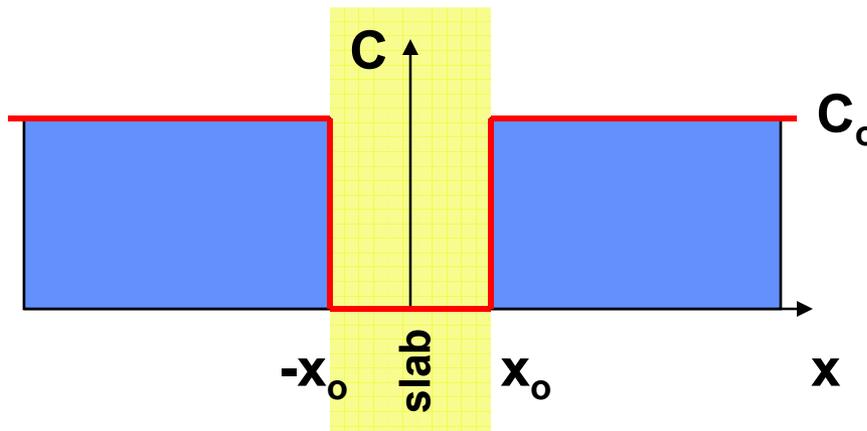
**note Dt has units of {length}$^2$**

# Boundary and initial conditions

- **general solution should look something like**

$$C(x, t) = A + \sum_n \exp\left(-D \cdot [k_n]^2 \cdot t\right) \cdot \left(E_n \cdot \cos[k_n \cdot x] + F_n \cdot \sin[k_n \cdot x]\right)$$
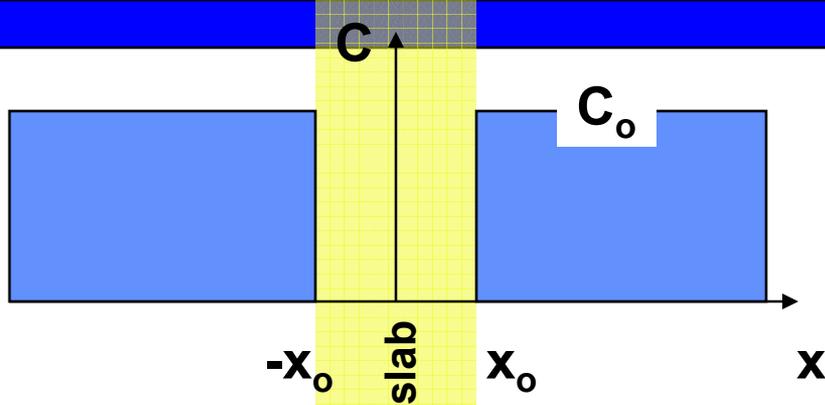
- **still need to find the constants**
  - **need to specify boundary and initial conditions to complete solution**
- **example: finite thickness undoped sheet surrounded by a "constant source" reservoir**



$$C(x, t = 0) = \begin{cases} C_o, & |x| < x_o \\ 0, & |x| > x_o \end{cases}$$

$$C(x_o, t) = C(-x_o, t) = C_o$$

$$C(x, t = 0) = A + \sum_n \left(E_n \cdot \cos[k_n \cdot x] + F_n \cdot \sin[k_n \cdot x]\right)$$

# Finite thickness slab

$$C(x, t = 0) \ = \ A + \sum_n \left( E_n \cdot \cos[k_n \cdot x] \ + \ F_n \cdot \sin[k_n \cdot x] \right)$$
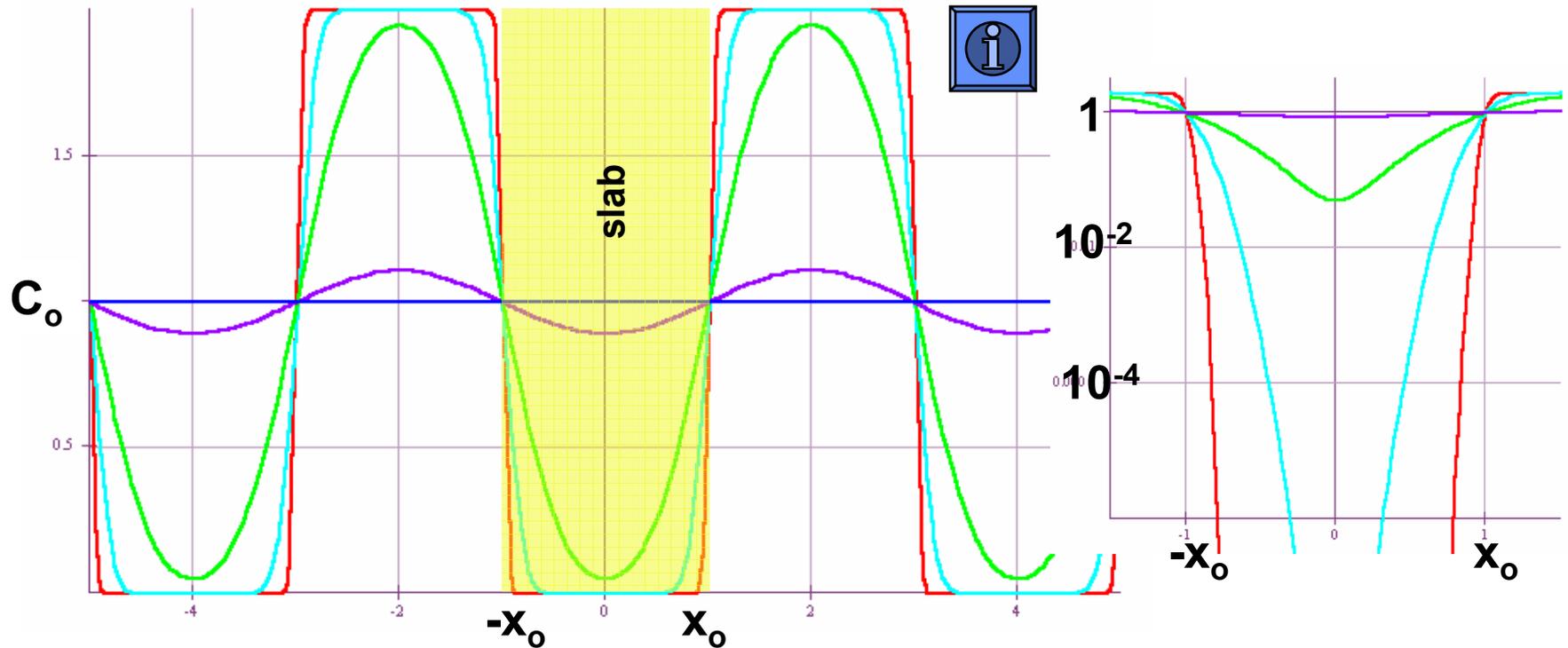
- **case: finite thickness, initially undoped slab, surrounded by "constant source" reservoirs of dopants**
  - **bc: external concentration NEVER changes**
- **this looks just like a Fourier series problem for a rectangular pulse, unit height**
  - **need to do "periodic extension", then find Fourier coefficients**
    - **yields simple rectangular pulse function, either sine or cosine series will be sufficient**
    - **pick cosine series**
  - **C(x = $x_o$, t = 0) = $C_o$  ➡  $k_n$ = odd integer $\cdot \pi$ / $2x_o$**

$$C_{slab}(x, \ t) \ = \ C_o \cdot \left\{ 1 + 4 \cdot \sum_{n=1}^{\infty} \exp\left( -D \cdot \left[ \frac{(2n-1) \cdot \pi}{2x_o} \right]^2 \cdot t \right) \cdot \left( \frac{(-1)^n}{(2n-1) \cdot \pi} \cdot \cos\left[ \frac{(2n-1) \cdot \pi}{2x_o} \cdot x \right] \right) \right\}$$

# Finite thickness slab

- **case: finite thickness, initially undoped slab, surrounded by "constant source" reservoirs of dopants**

$$C_{slab}(x,\ t)\ =\ C_o \cdot \left\{ 1 + 4 \cdot \sum_{n=1}^{\infty} \exp\left( -D \cdot \left[ \frac{(2n-1) \cdot \pi}{2x_o} \right]^2 \cdot t \right) \cdot \left( \frac{(-1)^n}{(2n-1) \cdot \pi} \cdot \cos\left[ \frac{(2n-1) \cdot \pi}{2x_o} \cdot x \right] \right) \right\}$$



- **units of time: $x_o^2/D$**

# How do you deal with an un-bounded medium?

$$\frac{\partial u}{\partial t} = D \cdot \frac{\partial^2 u}{\partial x^2}$$

$$\Longrightarrow \qquad X \cdot \frac{dT}{dt} = D \cdot T \cdot \left[\frac{d^2 X}{dx^2}\right]$$

$$u(x,\ t) = X(x) \cdot T(t)$$

$$\frac{1}{X} \cdot \frac{d^2 X}{dx^2} = -k^2 \qquad \frac{1}{T} \cdot \frac{dT}{dt} = -D \cdot k^2$$

**note Dt has units of {length}$^2$**

- **need to use Fourier transform rather than Fourier series**
  - **gives continuous "spectrum" of k values**
  - **integrate over k to get closed form expression**
- **in general, if the initial condition u(x, t = 0) is known for all x, then the final solution is given by**

$$u(x,\ t) = \frac{1}{2 \cdot \sqrt{\pi \cdot D \cdot t}} \cdot \int_{-\infty}^{+\infty} u(\xi,\ 0) \cdot e^{-[\xi\ -\ x]^2/4Dt}\ d\xi$$

# Infinite slab, initially "half-doped"

- **example:**
  - **uniform medium extending from x = - ∞ to x = + ∞**
  - **initial concentration**
    - **for x < 0 : $C(x<0, t = 0) = 2 \cdot C_o$**
    - **for x > 0 : $C(x>0, t = 0) = 0$**
  - **at t = ∞ the solution should be a constant everywhere = $C_o$**

$$C(x, t) = \frac{1}{2 \cdot \sqrt{\pi \cdot D \cdot t}} \cdot \int_{-\infty}^{+\infty} \begin{cases} 2 \cdot C_o , \xi < 0 \\ 0 \qquad , \xi > 0 \end{cases} \cdot e^{-[\xi - x]^2 / 4Dt} \, d\xi$$

$$C(x, t) = \frac{1}{2 \cdot \sqrt{\pi \cdot D \cdot t}} \cdot \left[ \int_{-\infty}^{0} 2 \cdot C_o \cdot e^{-[\xi - x]^2 / 4Dt} \, d\xi + \int_{0}^{+\infty} 0 \cdot e^{-[\xi - x]^2 / 4Dt} \, d\xi \right]$$

$$z = \frac{\xi - x}{2\sqrt{D \cdot t}}$$

$$C(x, t) = \frac{1}{2 \cdot \sqrt{\pi \cdot D \cdot t}} \cdot \left[ \int_{-\infty}^{-x/2\sqrt{Dt}} 2 \cdot C_o \cdot e^{-\left[z \cdot 2\sqrt{Dt}\right]^2 / 4Dt} \left( 2\sqrt{D \cdot t} \, dz \right) \right]$$

$$C(x, t) = \frac{2 \cdot C_o \cdot \sqrt{D \cdot t}}{\sqrt{\pi \cdot D \cdot t}} \cdot \left[ \int_{x/2\sqrt{D \cdot t}}^{\infty} e^{-z^2} \, dz \right]$$
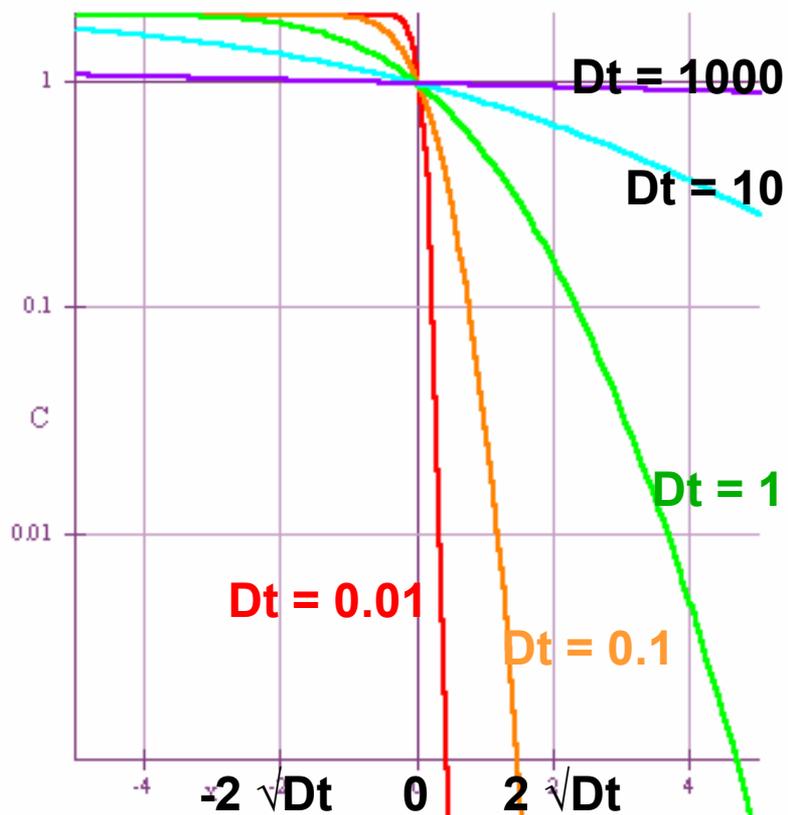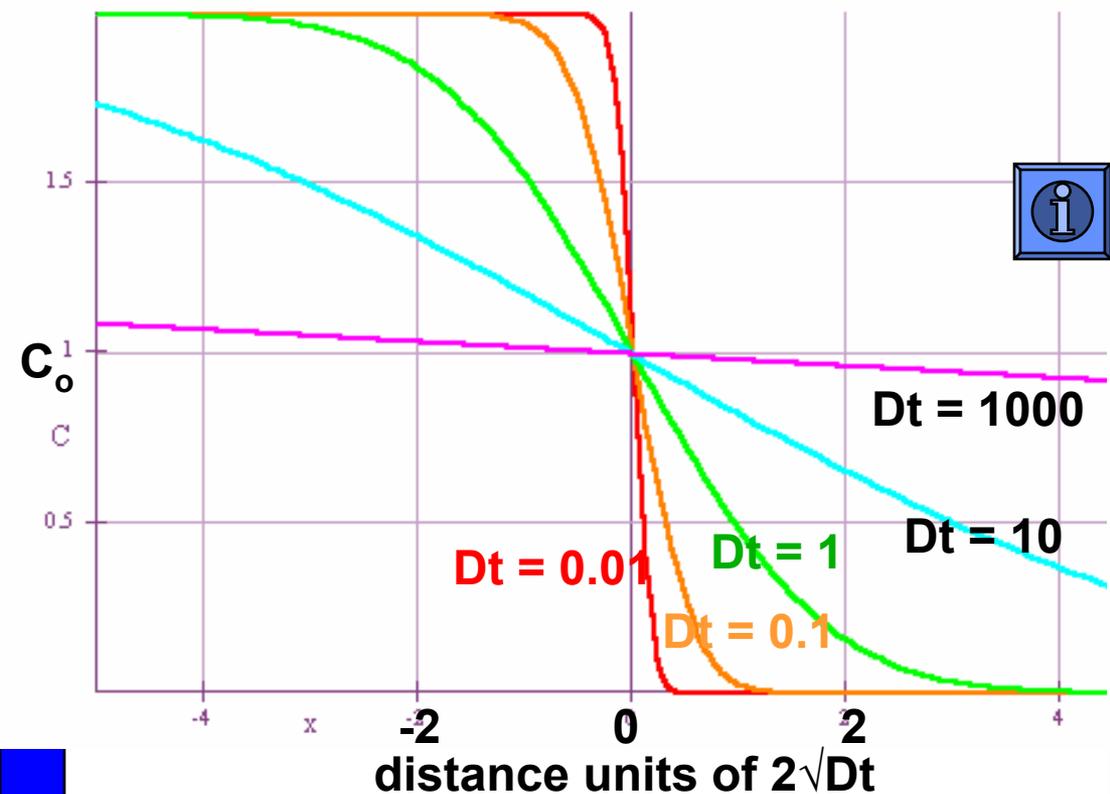
# Infinite slab, "half-doped"

- **example:**
  - **uniform medium extending from x = - ∞ to x = + ∞**
  - **initial concentration**
    - **for x < 0 : C(x<0, t = 0) = 2·C$_o$**
    - **for x > 0 : C(x>0, t = 0) = 0**

$$C(x, t) = \frac{2 \cdot C_o \cdot \sqrt{D \cdot t}}{\sqrt{\pi \cdot D \cdot t}} \cdot \left[ \int_{x/2\sqrt{D \cdot t}}^{\infty} e^{-z^2} \, dz \right]$$

$$\operatorname{erfc}(y) \equiv \frac{2}{\sqrt{\pi}} \int_y^{\infty} e^{-\xi^2} d\xi = 1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-\xi^2} d\xi = 1 - \operatorname{erf}(y)$$

$$C(x, t) = C_o \cdot \left[ \frac{2}{\sqrt{\pi}} \int_{x/2\sqrt{D \cdot t}}^{\infty} e^{-z^2} \, dz \right] = C_o \cdot \left[ \operatorname{erfc}\left( \frac{x}{2\sqrt{D \cdot t}} \right) \right]$$
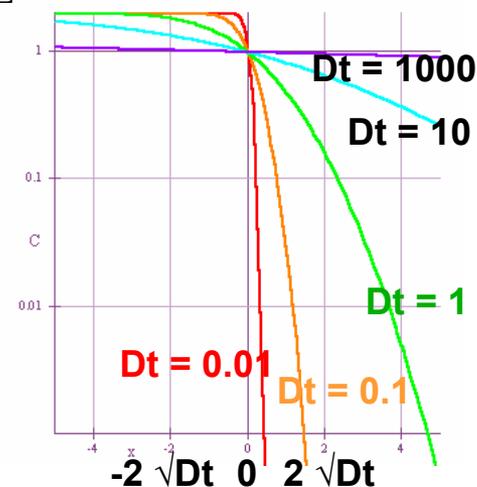
# Infinite slab, "half-doped"

- **example: uniform medium extending from x = - ∞ to x = + ∞**
- **initial concentration C(x<0, t = 0) = 2·C$_o$ ; C(x>0, t = 0) = 0**

$$C(x, \, t) \; = \; C_o \cdot \left[ \frac{2}{\sqrt{\pi}} \int\limits_{x/2\sqrt{D \cdot t}}^{\infty} e^{-z^2} \; dz \right] \; = \; C_o \cdot \left[ \mathrm{erfc}\left( \frac{x}{2\sqrt{D \cdot t}} \right) \right]$$

$\dfrac{C}{C_o}$

**Dt = 1000**

**Dt = 10**

**Dt = 1**

**Dt = 0.01**

**Dt = 0.1**

**distance units of 2√Dt**

**Dt = 1000**

**Dt = 10**

**Dt = 1**

**Dt = 0.01**

**Dt = 0.1**

**-2 √Dt**   **0**   **2 √Dt**

# Boundary/initial conditions: constant source diffusion into a "half-space"

- **initial conditions**
  - **N(x, 0) = 0  (no dopants in sample)**
- **boundary conditions (sample extends from x = 0  to x = + $\infty$)**
  - **N(0, t) = $N_S$, a constant**
  - **N($\infty$, t) = 0 (dopants never make it to the "back" of the wafer)**
- **we've already solved this one: see the last slide!**
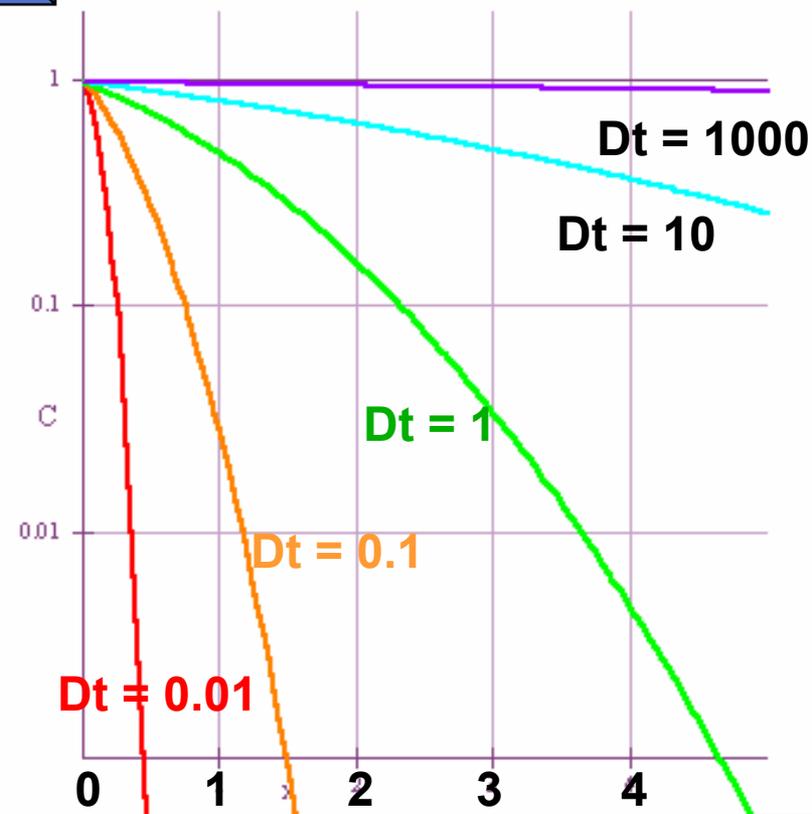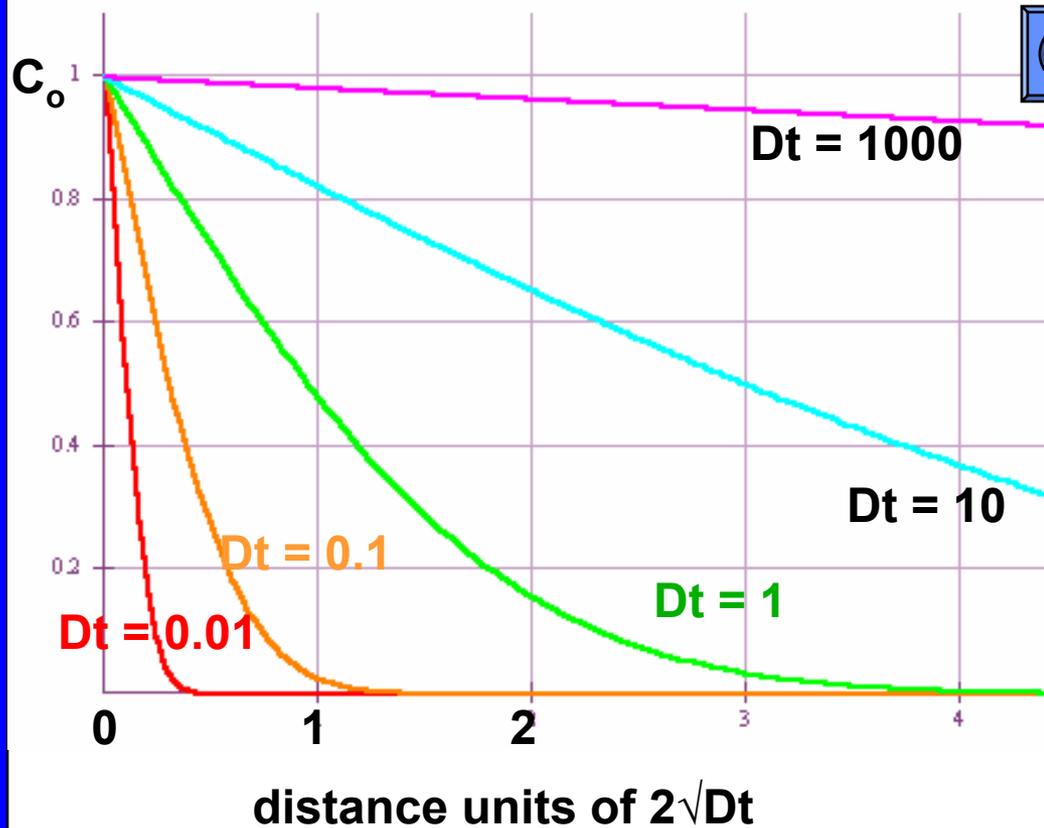  - **solution is a complimentary error function**

$$N(x,t) = N_S \, \text{erfc}\left(\frac{x}{2\sqrt{D\,t}}\right) \qquad \text{erfc}(y) = 1 - \frac{2}{\sqrt{\pi}}\int_0^y \exp\left(-z^2\right)dz$$

  - **note argument is x/2√Dt**

- **examples**
  - **pre-deps**
  - **high surface concentration diffusions**
    - **ohmic contacts**
    - **emitters**



Dt = 1000
Dt = 10
Dt = 1
Dt = 0.01
Dt = 0.1
-2 √Dt   0   2 √Dt

# "pre-dep" profiles

- **simple erfc result**



$C_o$

Dt = 1000

Dt = 10

Dt = 1

Dt = 0.1

Dt = 0.01

**distance units of 2√Dt**

Dt = 1000

Dt = 10

Dt = 1

Dt = 0.1

Dt = 0.01

# Solid solubility limits

- **for various impurities in silicon**
  - **note that solubility grows as T increases, peaks, then falls as T nears the melting point (1420°C)**
- **adapted from Ghandhi, 2nd ed. p. 90**
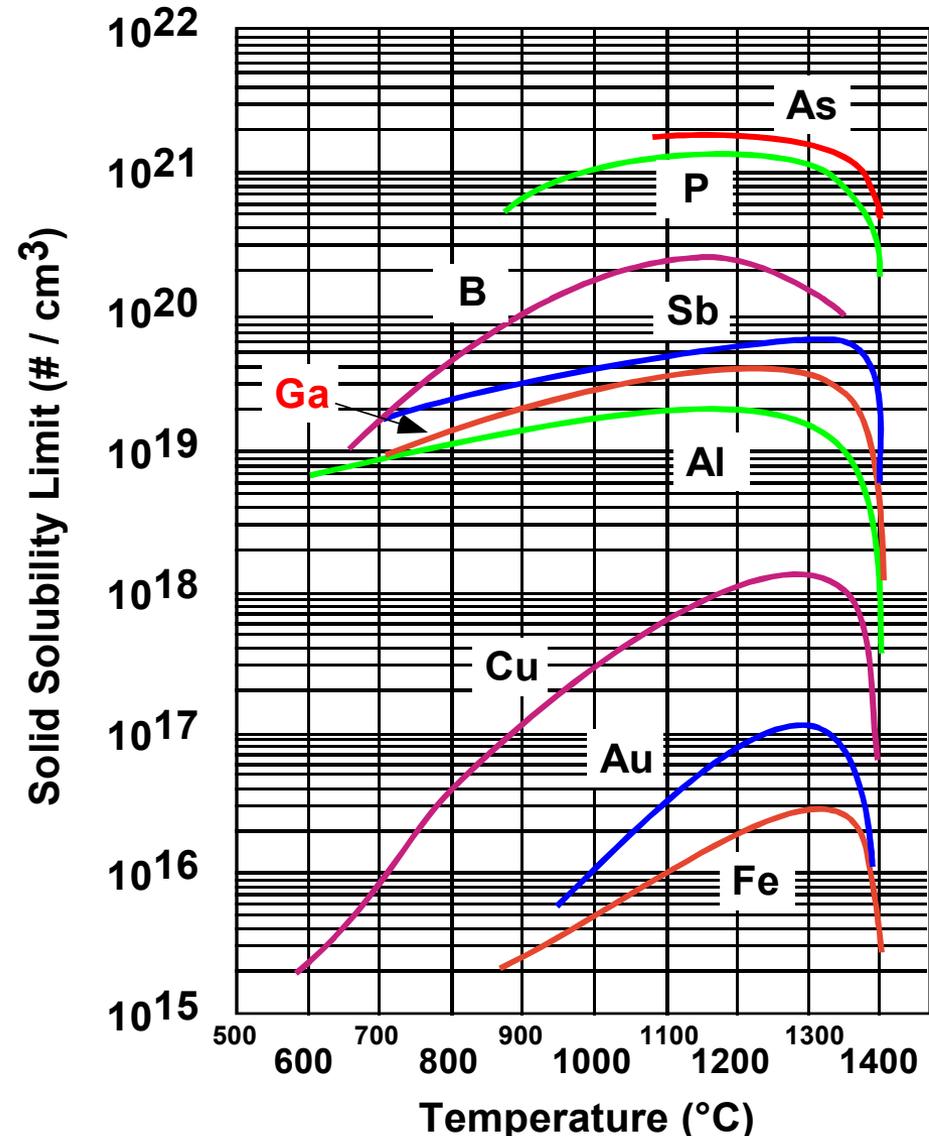
# Boundary/initial conditions: limited source diffusion into an unbounded medium

- **initial condition**
    - $N(x, 0) = 2Q_o\delta(x)$ **(all dopants initially at x = 0)**
        - **$2Q_o$ is the TOTAL dose, #/cm$^2$**
        - **at all times t**
        $$\int_{-\infty}^{\infty} N(x',t)\,dx' = 2Q_o$$

- **now apply our transform result**

$$N(x,\ t)\ =\ \frac{1}{2\cdot\sqrt{\pi\cdot D\cdot t}}\cdot\int_{-\infty}^{+\infty} 2Q_o\cdot\delta(\xi)\cdot e^{-[\xi-x]^2/4Dt}\ d\xi\ \ =\frac{Q_o}{\sqrt{\pi\cdot D\cdot t}}\cdot e^{-x^2/4Dt}$$

- **so solution is a gaussian**

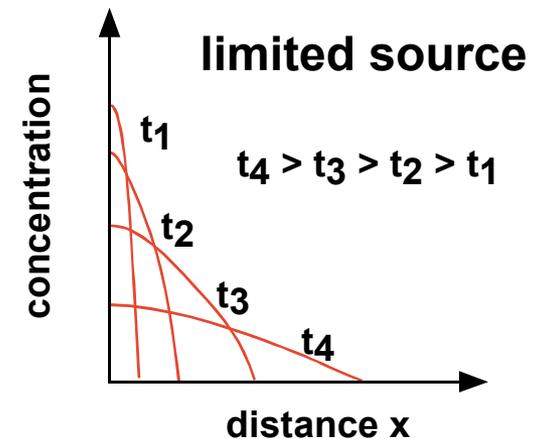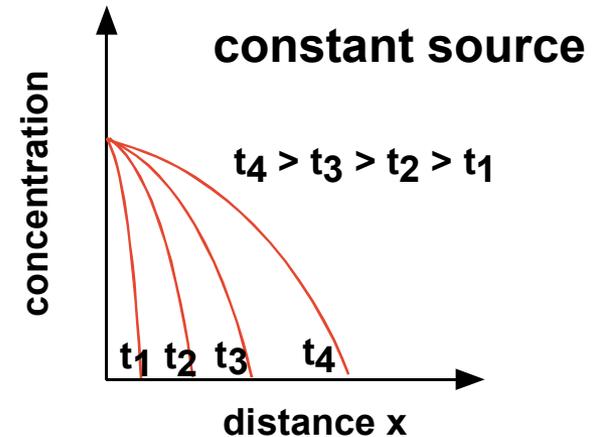$$N(x,t) = \frac{Q_o}{\sqrt{\pi\,Dt}}\ \textbf{exp}\left(-\left[\frac{x}{2\sqrt{Dt}}\right]^2\right)$$

- **note argument is x/2√Dt**
    - **$N_{peak} = Q_o\ /\ \sqrt{\pi Dt}$**
- **examples**
    - **drive-ins**
    - **low surface concentration, deep diffusions**
        - **CMOS n, p – wells; bipolar base**

# Constant diffusivity results

- solutions to the diffusion equation
  - "constant source"
    - unlimited supply of impurities
    - erfc shape
  - "limited source"
    - fixed number of impurities initially located at surface of sample
    - gaussian shape
  - diffusion length:

$$l \approx \sqrt{D \cdot t} \qquad D \approx D_o e^{-E/kT}$$

  - D ~ 3 x 10$^{-14}$ cm$^2$ sec$^{-1}$ @ 1300K
  - l ~ 0.1 $\mu$m @ one hour



constant source

$t_4 > t_3 > t_2 > t_1$



limited source

$t_4 > t_3 > t_2 > t_1$

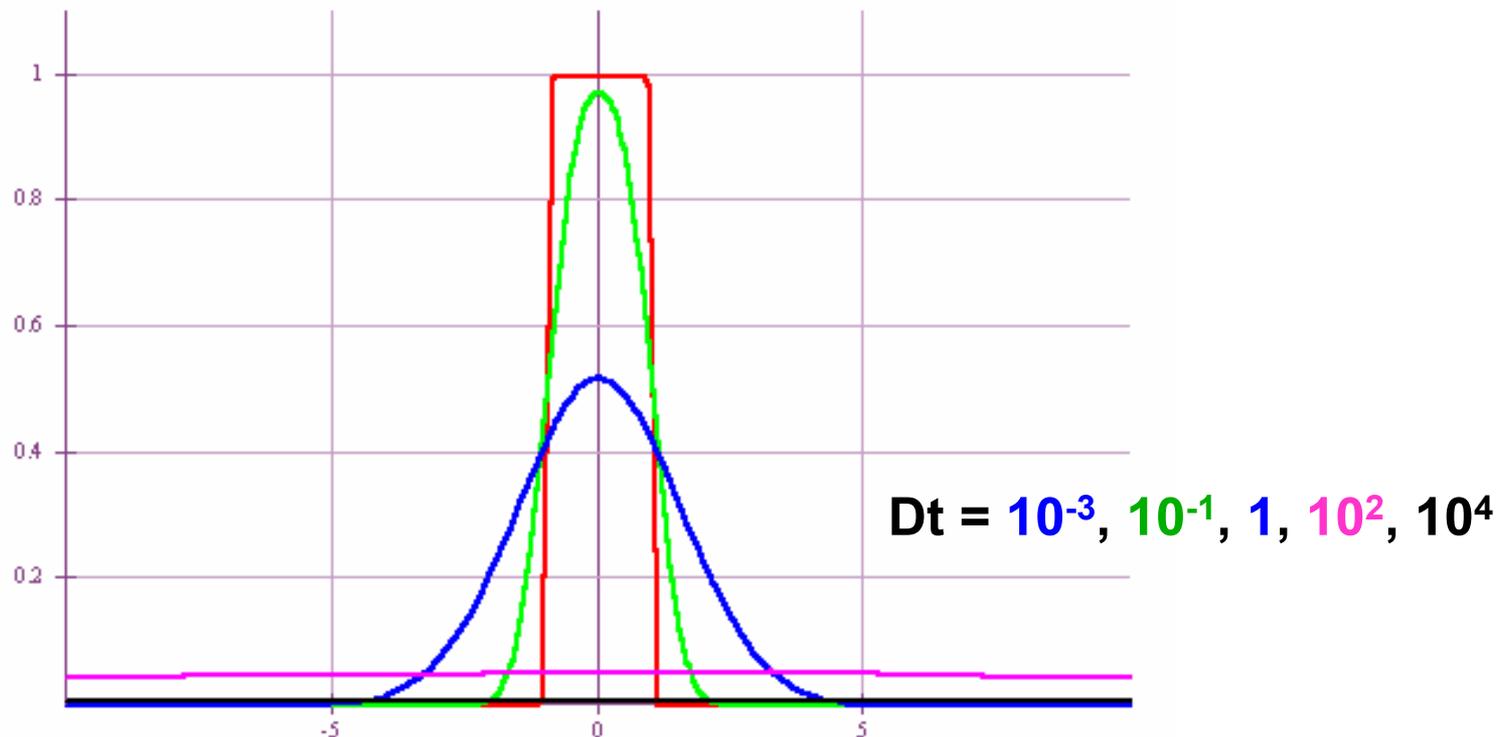# gaussian and erfc profiles
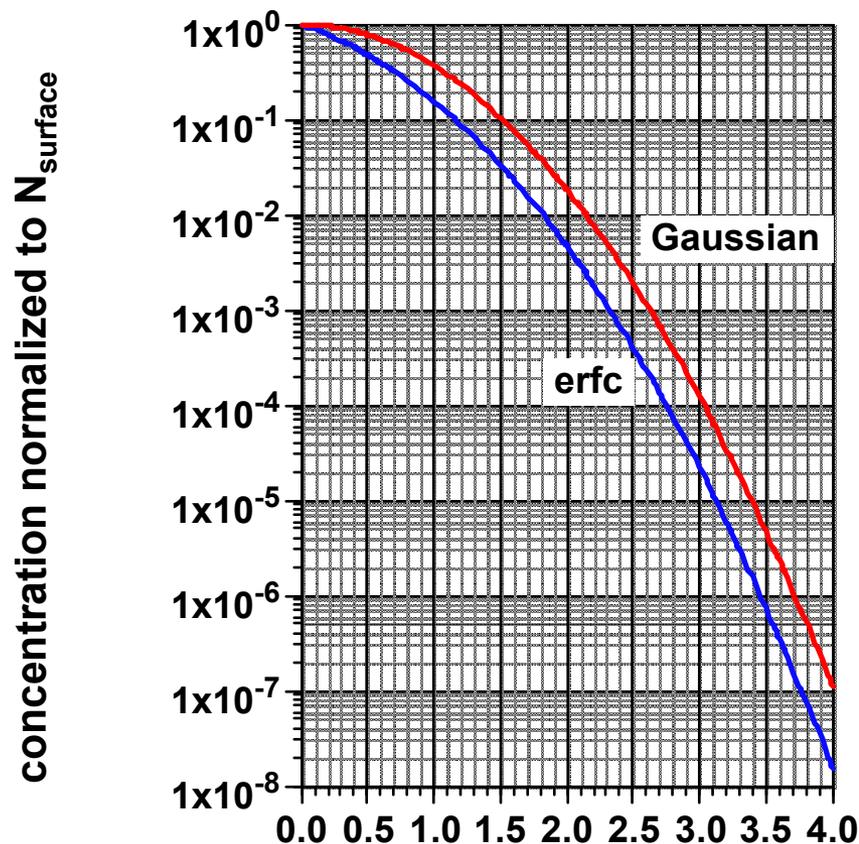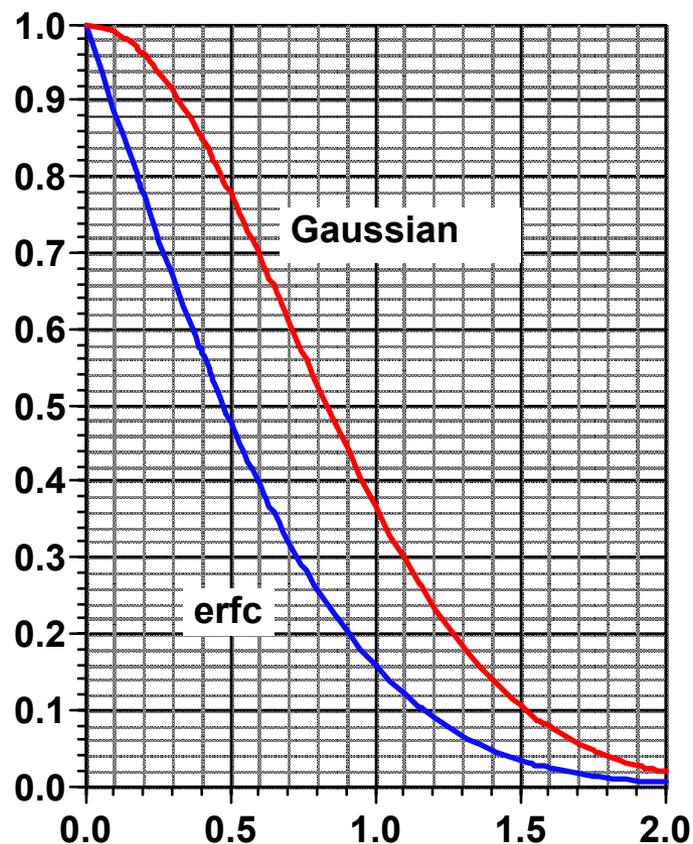


**argument "z" = x / 2$\sqrt{Dt}$**

# Slab out-diffusion

- **diffusion from finite thickness doped region (located from $-x_o$ to $x_o$), diffusing out into undoped material**

$$C(x,\ t)\ =\ \frac{C_o}{2} \cdot \left\{ \text{erfc}\left[ \frac{(x_o\ -\ x)}{2\sqrt{Dt}} \right]\ +\ \text{erfc}\left[ \frac{(x_o\ +\ x)}{2\sqrt{Dt}} \right] \right\}$$



**Dt = $10^{-3}$, $10^{-1}$, 1, $10^{2}$, $10^{4}$**

# How do you handle multiple steps?

- **for several sequential "diffusions"**
  - **if the same BC's and temperature, then its easy**
    - **just add the times to get $D \cdot (t_1 + t_2)$**
  - **what if the temperatures change?**
    - **example: gaussian profile "started" as a delta function, but after time $\delta t$, it's a gaussian**
      - **$\Rightarrow$ a gaussian profile must transform into a gaussian!**
    - **$\Rightarrow$ first time/temp. step generates a gaussian, serves as initial condition for second gaussian**
      - **$\Rightarrow$ add: $D_1 \cdot t_1 + D_2 \cdot t_2$**

$$N(x,t) = \frac{Q_o}{\sqrt{\pi(D_1 t_1 + D_2 t_2)}} \exp\left(-\left[\frac{x}{2\sqrt{(D_1 t_1 + D_2 t_2)}}\right]^2\right)$$

- **hard to do anything easy for a constant source diffusion**

# Two-step diffusion profile

- **first step ($t < t_1$) is constant source, surface concentration $N_{01}$**
  - **pre-dep**
- **second step ($t_1 < t < t_1 + t_2$) is limited source**
  - **drive-in**
- **profile is a "Smith integral"**
  - **surface concentration is**
  - **limits**

$$N_{surface} = \frac{2\,N_{01}}{\pi}\,\tan^{-1}\left(\sqrt{\frac{D_1\,t_1}{D_2\,t_2}}\right)$$

- **$D_1 t_1 \gg D_2 t_2$   (long pre-dep)**

$$\tan^{-1}\left(\sqrt{\frac{D_1\,t_1}{D_2\,t_2}} \gg 1\right) \approx \frac{\pi}{2} \quad \Rightarrow \quad N_{surface} \approx \frac{2\,N_{01}}{\pi}\,\frac{\pi}{2} = N_{01}$$

- **$D_1 t_1 \ll D_2 t_2$    (long drive-in)**

$$\tan^{-1}\left(\sqrt{\frac{D_1 t_1}{D_2 t_2}} \ll 1\right) \approx \sqrt{\frac{D_1 t_1}{D_2 t_2}} \quad \Rightarrow \quad N_{surface} \approx \frac{2 N_{01}}{\pi}\sqrt{\frac{D_1 t_1}{D_2 t_2}}$$

  - **recall drive-in result**

$$N_{surf} = \frac{Q_o}{\sqrt{\pi D_{(2)} t_{(2)}}} \quad \Leftrightarrow \quad \frac{2 N_{01}}{\pi}\sqrt{\frac{D_1 t_1}{D_2 t_2}}$$
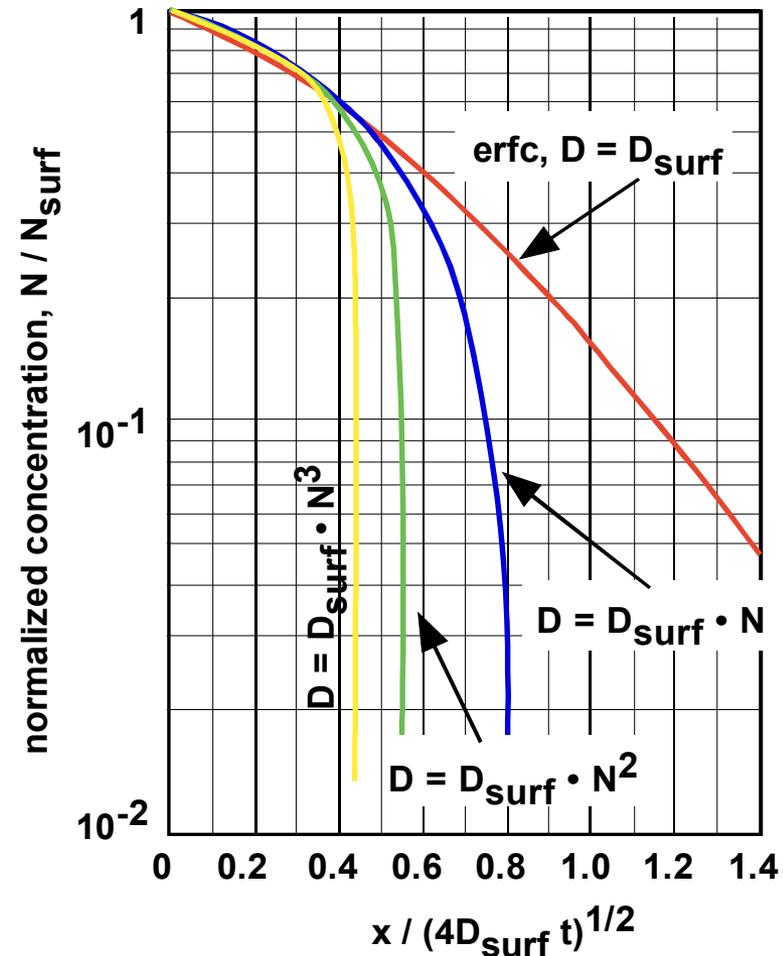
$$\Rightarrow \quad Q_o^{effective} = \frac{2 N_{01}}{\sqrt{\pi}}\sqrt{D_1 t_1}$$

# Concentration dependent D profiles

- **"high" concentration**
  - **must solve**

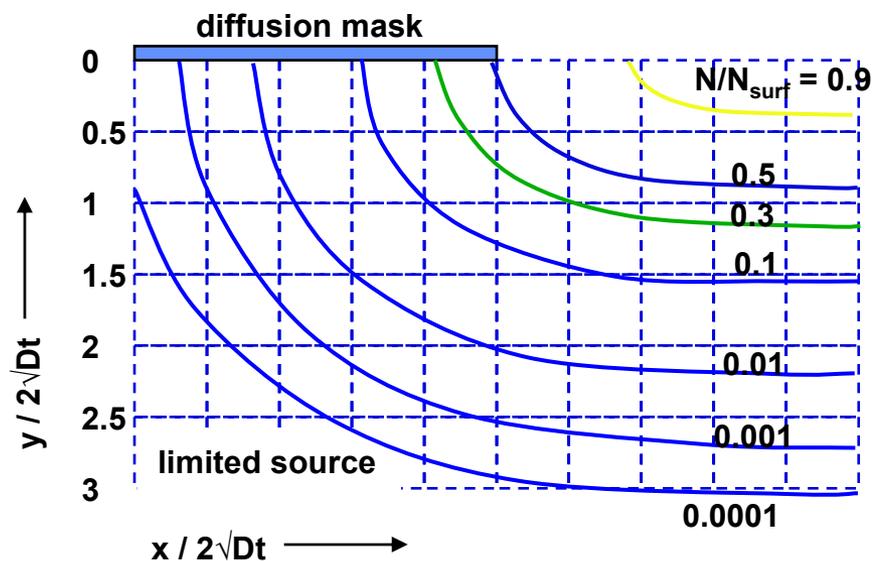$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial x}\left( D\frac{\partial N}{\partial x} \right)$$

  - **normally requires numerical solution**

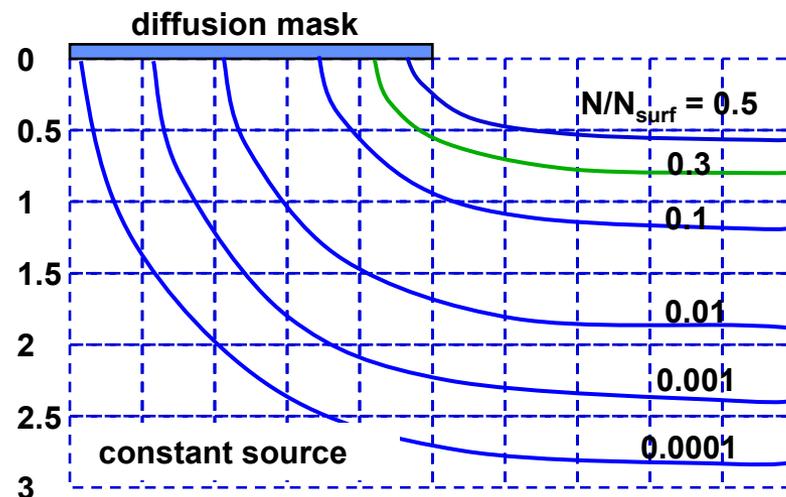  - **note that as $N < n_i$ D goes to a constant!!**

adapted from Ghandhi, 2nd edition, p. 181

# Diffusion in two dimensions

- **at mask edge have 2-D behavior**
  - **diffuses laterally ~ 75 - 80 % of depth**



**adapted from Ghandhi, 2nd edition, p. 183**

# Finding junction depth

example:
$N_B/N_{surf} = 3 \times 10^{-5}$

$\Rightarrow$ $z_{erfc} \approx 2.9$ $\Rightarrow$ $x_j^{erfc} \approx 2.9(2\sqrt{Dt})$

example:
$N_B/N_{surf} = 3 \times 10^{-5}$

$\Rightarrow$ $z_{gauss} \approx 3.2$ $\Rightarrow$ $x_j^{gauss} \approx 3.2(2\sqrt{Dt})$



$N_{backgrnd}/N_{surface}$

Gaussian
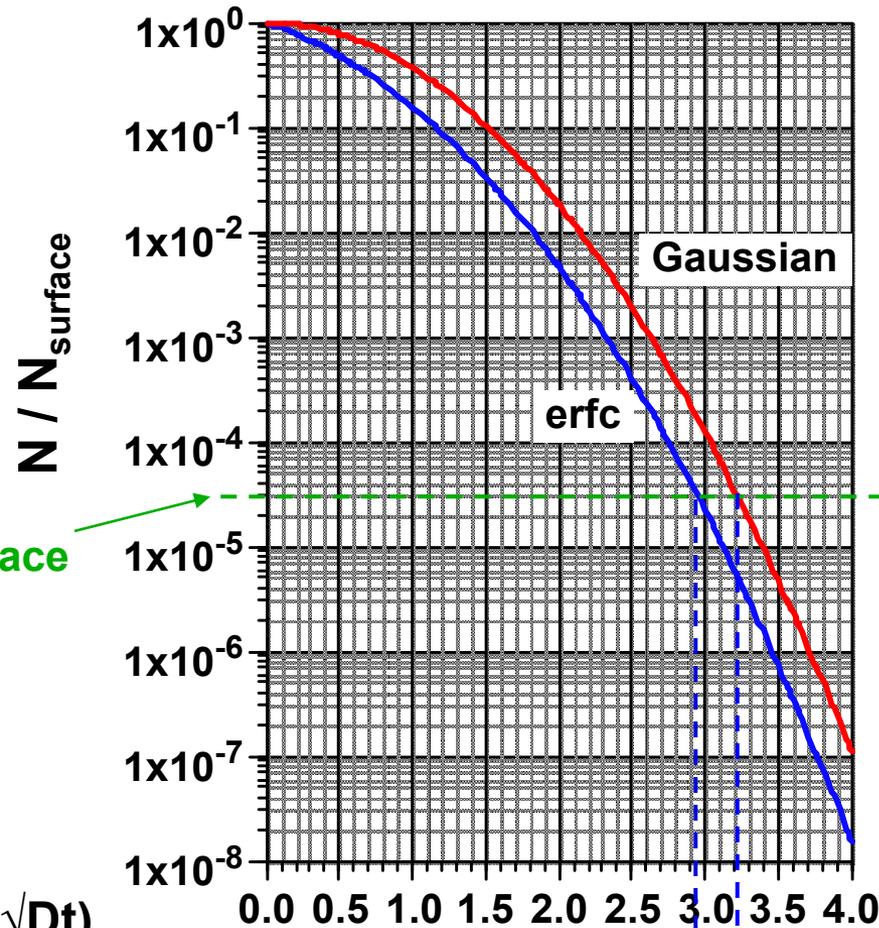
erfc

$z_{erfc} \approx 2.9$ $z_{gauss} \approx 3.2$

argument "z" = $x / 2\sqrt{Dt}$

# Diffusion Systems

- **typical diffusion furnace controlled to ± 1 /2° C in 600 - 1200° C range**
- **usually transport the oxide of impurity to silicon, react there to form free impurity and $SiO_2$**
- **surface concentration usually set by solid solubility limit (may not all be electrically active)**
- **transport mechanisms:**
  - **spin - on glass**
  - **solid source**
  - **liquid source or gas source or gas source stream**
  - **best control over doping concentrations (dose) usually only ~ 5 -10 %**
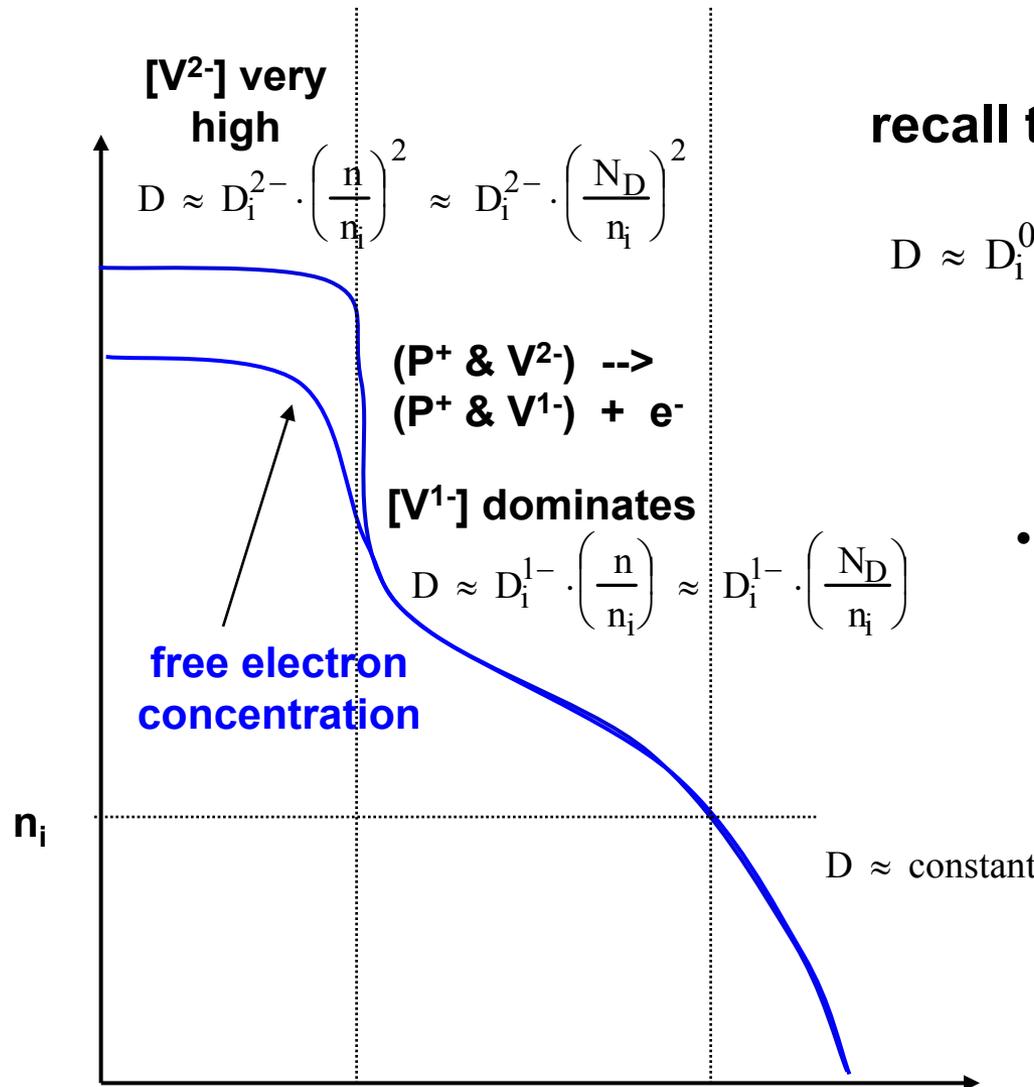
# Boron in silicon

- **maximum surface concentration set by solid solubility**
  - @ 1100° C : $N_{ss} \approx 4 \times 10^{20}$ cm$^{-3}$
  - only about $2 \times 10^{20}$ are active
- **transport of oxide to silicon surface**
  - $2B_2O_3 + 3Si \; --> \; 4B + 3SiO_2$
  - how much oxide does this make?
    - dose $Q_o \sim 10^{15}$ cm$^{-2}$ (this is a lot!) --> only about one "atomic layer" of $SiO_2$
- **sources**
  - solid: oxidized boron nitride
  - liquid: trimethylborate (TMB)
  - gas: diborane
  - all react in furance gas stream to produce $B_2O_3$
- **potential problem: "boron skin"**

# Phosphorus in silicon

- **maximum surface concentration set by solid solubility**
  - **@ 1100° C : $N_{ss} \approx 10^{21}$ cm$^{-3}$**
  - **only about $3 \times 10^{20}$ are active**
- **transport of oxide to silicon surface**
  - **$2P_2O_5 + 5Si \; --> \; 4P + 5SiO_2$**
- **sources**
  - **solid: silicon pyrophosphate in inert binder**
  - **liquid: phosphorus oxychloride $POCl_3$**
  - **gas: phosphine $PH_3$**
  - **all react in furnace gas stream to produce $P_2O_5$**
- **potential problems**
  - **anomalous diffusion profiles**
  - **emitter-push effect**

# Anomalous phosphorus diffusion

**[V$^{2-}$] very high**

$$D \approx D_i^{2-} \cdot \left(\frac{n}{n_i}\right)^2 \approx D_i^{2-} \cdot \left(\frac{N_D}{n_i}\right)^2$$

**(P$^+$ & V$^{2-}$) --> (P$^+$ & V$^{1-}$) + e$^-$**

**[V$^{1-}$] dominates**

$$D \approx D_i^{1-} \cdot \left(\frac{n}{n_i}\right) \approx D_i^{1-} \cdot \left(\frac{N_D}{n_i}\right)$$

**free electron concentration**

$n_i$

$D \approx constant$

**recall that for phosphorus**

$$D \approx D_i^0 + D_i^{1-} \cdot \frac{n}{n_i} + D_i^{2-} \cdot \left(\frac{n}{n_i}\right)^2$$

- **"kink" in profile associated with interaction between P$^+$ and charged defects**

# Emitter push effect

- **also associated with phosphorus diffusion**
  - **high concentration diffusion of phosphorus alters vacancy concentrations**
    - **vacancies have very high diffusivity!**
  - **"excess" vacancies can interact with other impurities that may already be present**
    - **enhances boron diffusion, causes base to "dip"**



**without emitter push**  **phosphorus**

**boron**

$\delta$

**with emitter push**
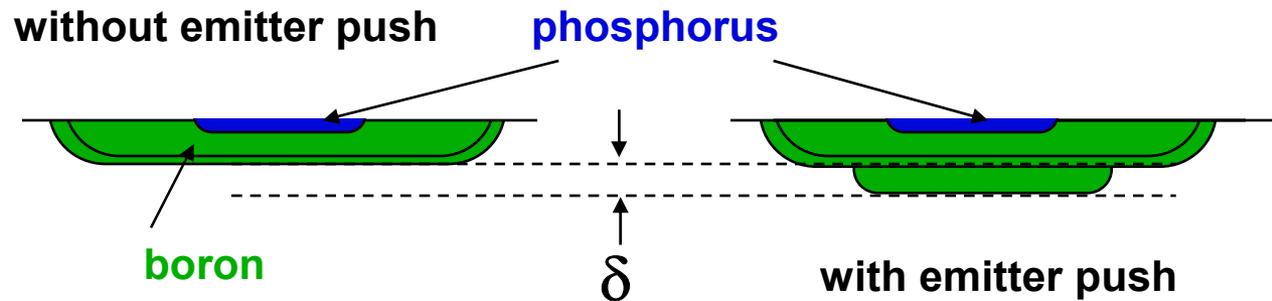
# Ion Implantation

- **alternative to diffusion for the introduction of dopants**
- **essentially a "physical" process, rather than "chemical"**
- **advantages:**
  - **mass separation allows wide varies of dopants**
  - **dose control:**
    - **diffusion 5 - 10%**
    - **implantation:**
      - $10^{11}$ - $10^{17}$ **ions / cm$^2$ ± 1 %**
      - $10^{14}$ - $10^{21}$ **ions / cm$^3$**
  - **low temperature**
  - **tailored doping profiles**

# Diffusion with spherical symmetry

- **Fick's 1st law:**

$$\vec{j} = D \cdot \vec{\nabla} C = \underbrace{\hat{r} \cdot D \cdot \frac{\partial C}{\partial r}}_{\text{spherical symmetry}}$$

- **apply continuity equation**

$$- \overbrace{\vec{\nabla} \bullet \vec{j}}^{\substack{\text{spatial rate} \\ \text{of change} \\ \text{of flux}}} = \overbrace{\frac{\partial C}{\partial t}}^{\substack{\text{time rate} \\ \text{of change} \\ \text{of particle} \\ \text{accumulation}}}$$

- **yields Fick's 2nd law**

$$\frac{\partial C}{\partial t} = \vec{\nabla} \bullet \left( D \cdot \vec{\nabla} C \right)$$

  - **divergence in spherical coordinates**

$$\vec{\nabla} \bullet \vec{A} = \underbrace{\frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left( r^2 \cdot A_r \right)}_{\text{spherical symmetry}}$$

- **with spherical symmetry problem is 1-D**

$$\frac{\partial C}{\partial t} = \underbrace{\frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left( r^2 \cdot D \cdot \frac{\partial C}{\partial r} \right)}_{\text{spherical symmetry}}$$

# Spherical diffusion equation

- **looks exactly like 1-d problem, except solution is for the function u = r · C(r,t)**

- **general solution to the diffusion equation for infinite medium:**
  - **requires only initial condition**
  - **must be careful about "infinite medium condition"**
    - **use "reflection" to handle half-space diffusion**

$$\frac{\partial u}{\partial t} = D \cdot \frac{\partial^2 u}{\partial r^2} \qquad u(r,\, t) = \frac{1}{2 \cdot \sqrt{\pi \cdot D \cdot t}} \cdot \int_{-\infty}^{+\infty} u(\xi, 0) \cdot e^{-[\xi - r]^2 / 4Dt}\, d\xi$$

$$C(r,\, t) = \frac{C_o}{\sqrt{\pi}} \cdot \left\{ \frac{\sqrt{Dt}}{r} \left( e^{-\frac{(R-r)^2}{4Dt}} - e^{-\frac{(R+r)^2}{4Dt}} \right) + \frac{\sqrt{\pi}}{2} \left( \mathrm{erfc}\left[ \frac{(R-r)}{2\sqrt{Dt}} \right] + \mathrm{erfc}\left[ \frac{(R+r)}{2\sqrt{Dt}} \right] \right) \right\}$$