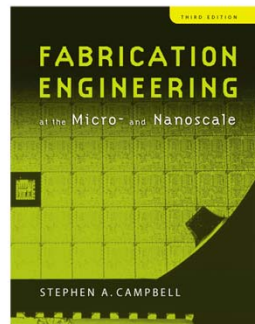


ECE 416/516 IC Technologies Lecture 3: Diffusion

Professor James E. Morris
Spring 2012

Chapter 3

Diffusion



Fabrication Engineering at the Micro- and Nanoscale

Campbell

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Doping Methods

Spin-on doped glass

Solid

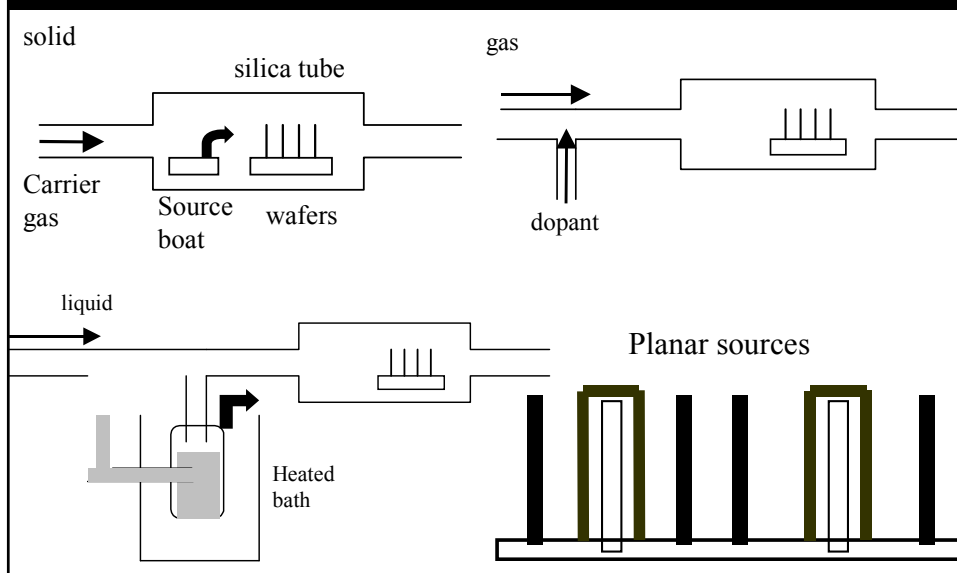
Liquid (bubbler)

Gaseous

Ion Implant

Planar Sources

Doping Methods

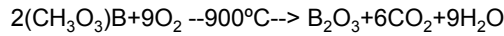


Boron & Phosphorus Doping

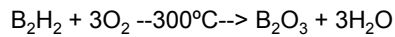
Boron



Liquid:

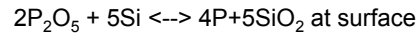


Gaseous:

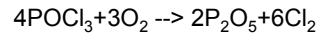


TMB - trimethylbromate

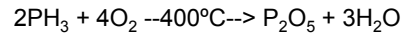
Phosphorus



Liquid:

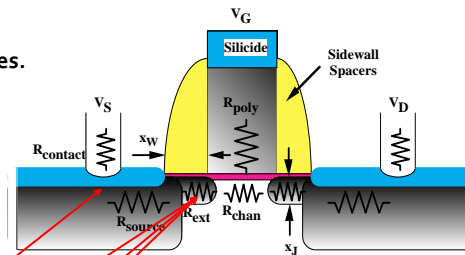


Gaseous:



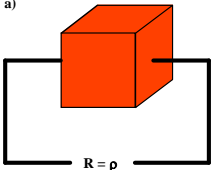
DIFFUSION

- Doping profiles determine many short-channel characteristics in MOS devices.
- Resistance impacts drive current.
- Scaling implies all lateral and vertical dimensions scale by the same factor.
- Generally doping levels need to increase and x_j values need to decrease.



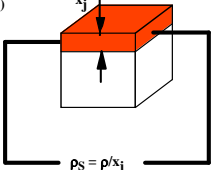
Year of Production	1998	2000	2002	2004	2007	2010	2013	2016	2018
Technology Node (half pitch)	250 nm	180 nm	130 nm	90 nm	65 nm	45 nm	32 nm	22 nm	18 nm
MPU Printed Gate Length		100 nm	70 nm	53 nm	35 nm	25 nm	18 nm	13 nm	10 nm
Contact Resistivity r_c ($\Omega \cdot \text{cm}^2$)			2×10^{-7}	1.6×10^{-7}	1×10^{-7}	6×10^{-8}	1.7×10^{-8}	8.7×10^{-9}	5×10^{-9}
S/D Extension Abruptness (nm/decade)				4.1	2.8	TBD	TBD	TBD	TBD
S/D Extension Sheet Resistance (PMOS) (Ω / sq)				660	890	1875	510	550	580
S/D Extension x_j (nm)	50-100	42-70	25-43	20	14	7.2	10	7.2	5.1
Min Supply Voltage (volts)	1.8-2.5	1.5-1.8	1.2-1.5	0.9-1.2	0.8-1.1	0.7-1.0	0.6-0.9	0.5-0.8	0.5-0.7

a)



$R = \rho$

b)



$\rho_s = \rho/x_j$

- The resistivity of a cube is given by

$$J = nqv = nq\mu E = \frac{1}{\rho} E \quad \therefore \rho = \frac{E}{J} \quad \Omega\text{cm} \quad (1)$$

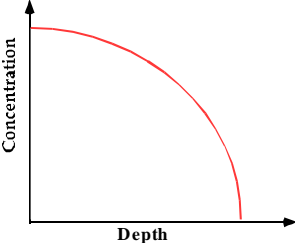
- The sheet resistance of a shallow junction is

$$R = \frac{\rho}{x_j} \Omega/\text{Square} \equiv \rho_s \quad (2)$$

- For a non-uniformly doped layer,

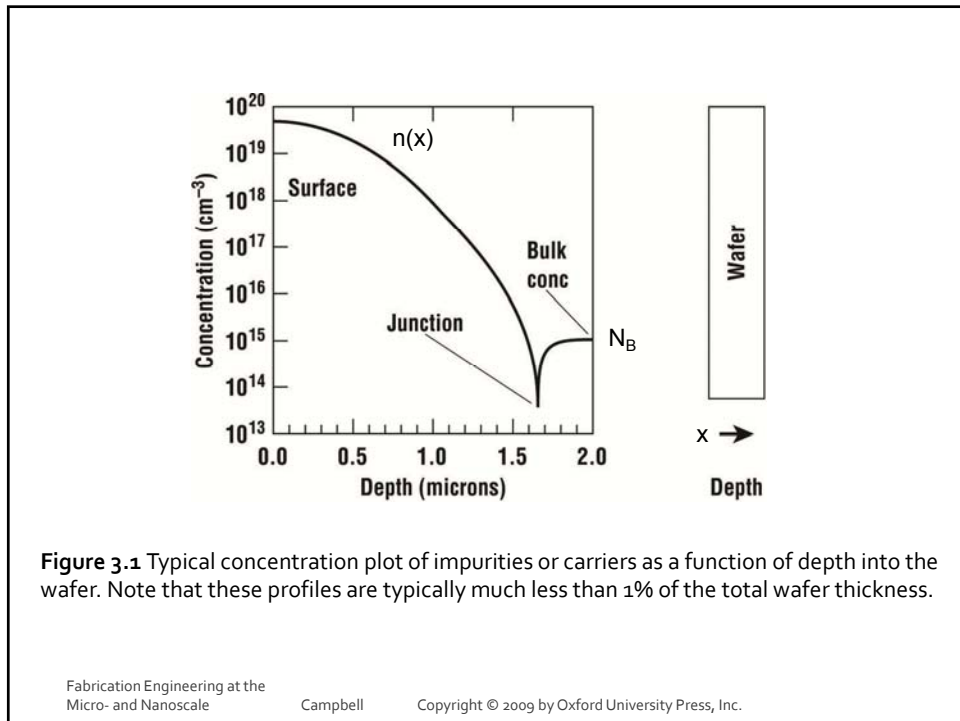
$$\rho_s = \frac{\rho}{x_j} = \frac{1}{q \int_0^{x_j} [n(x) - N_B] \mu dx} \quad (3)$$

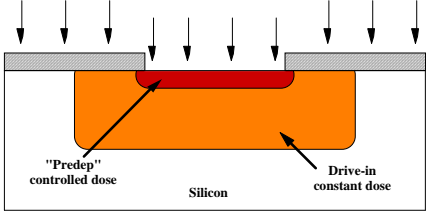
- Eqn. (3) has been numerically integrated by Irvin for simple analytical profiles (example later).



- Sheet resistance can be experimentally measured by a four point probe technique.
- Doping profiles can be measured by SIMS (chemical) or spreading R (electrical).

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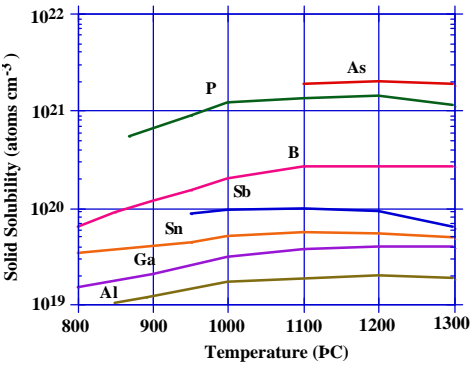




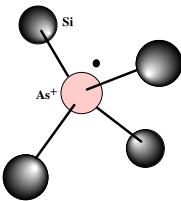
- Diffusion is the redistribution of atoms from regions of high concentration of mobile species to regions of low concentration. It occurs at all temperatures, but the diffusivity has an exponential dependence on T.
- **Predeposition:** doping often proceeds by an initial predep step to introduce the required dose of dopant into the substrate.
- **Drive-In:** a subsequent drive-in anneal then redistributes the dopant giving the required x_j and surface concentration.

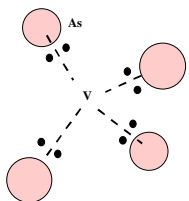
	Ion Implantation and Annealing	Solid/Gas Phase Diffusion
Advantages	Room temperature mask	No damage created by doping
	Precise dose control	Batch fabrication
	$10^{11} - 10^{16}$ atoms cm^{-2} doses	
	Accurate depth control	
Problems	Implant damage enhances diffusion	Usually limited to solid solubility
	Dislocations caused by damage may cause junction leakage	Low surface concentration hard to achieve without a long drive-in
	Implant channeling may affect profile	Low dose predepos very difficult

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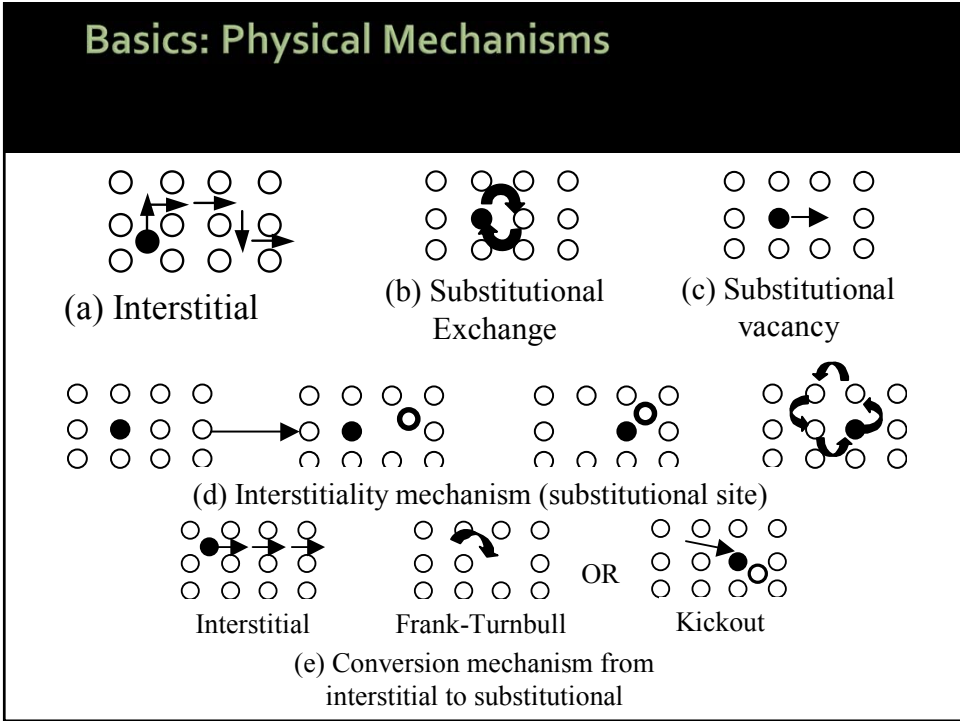
- Dopants are soluble in bulk silicon up to a maximum value before they precipitate into another phase.





- Dopants may have an "electrical" solubility that is different than the solid solubility defined above.
- One example - As_4V - electrically inactive complex.

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Physical Mechanism Notes

Dissociative mechanism:
 -generally mixture of interstitial and substitutional

Significant movement by interstitial only
 -substitutional requires adjacent vacancy

Interchange diffusion
 -Direct interchange $\circ \bullet \otimes \circ \circ$
 -Cooperative interchange: more than 2 atoms involved

Self-diffusion:
 -Lattice atoms also diffuse

Dislocation / Grain Boundary diffusion:
 -easier at crystal edges
 -Diffusion parallel to dislocation or along grain boundary
 -more than 3 orders faster than bulk

Interstitial

To move from one interstitial site to next, must "squeeze past" lattice atoms.
Requires energy E_m

So jump freq $\nu = 4 \nu_0 \exp - (E_m/kT)$

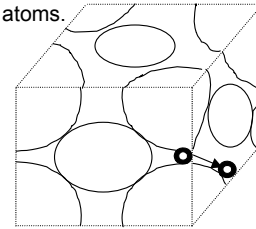
Vibr freq with $E > E_m$

4 adjacent sites for Si

Lattice vibration freq ν_0 ($10^{13} - 10^{14}$ / sec)

- Approx. 1 jump/minute at room temp.

(interstitial in Si)



e.g. FCC

Substitutional

Movement requires vacant site

- Schottky defect
- atom fraction: $\exp - (E_s/kT)$
- potential barrier: break bond E_n

$$\nu = 4\nu_0 (\exp - E_n/kT) (\exp - E_s/kT)$$

E_s to form vacancy less adjacent to impurity

- $E_n + E_s$ about 3-4eV for impurity diffusion
- $E_n + E_s = 5.13\text{eV}$ for Si self-diffusion

About 1 jump/ 10^{45} years at room temperature (compare interstitial one/min)

Mixed Diffusion

Impurities dissolve as both Substitutional & Interstitial

- Substitutional solubility N_s
- Interstitial solubility N_i
- Usually $N_s > N_i$ but $v_i \gg v_s$

Given atom spends (at equilibrium):

- $N_i / (N_i + N_s)$ time in interstitial site
- $N_s / (N_i + N_s)$ time in substitutional site

Therefore:

$$v_{\text{eff}} = (v_s N_s + v_i N_i) / (N_i + N_s)$$

$$\approx v_i / (1 + N_s / N_i)$$

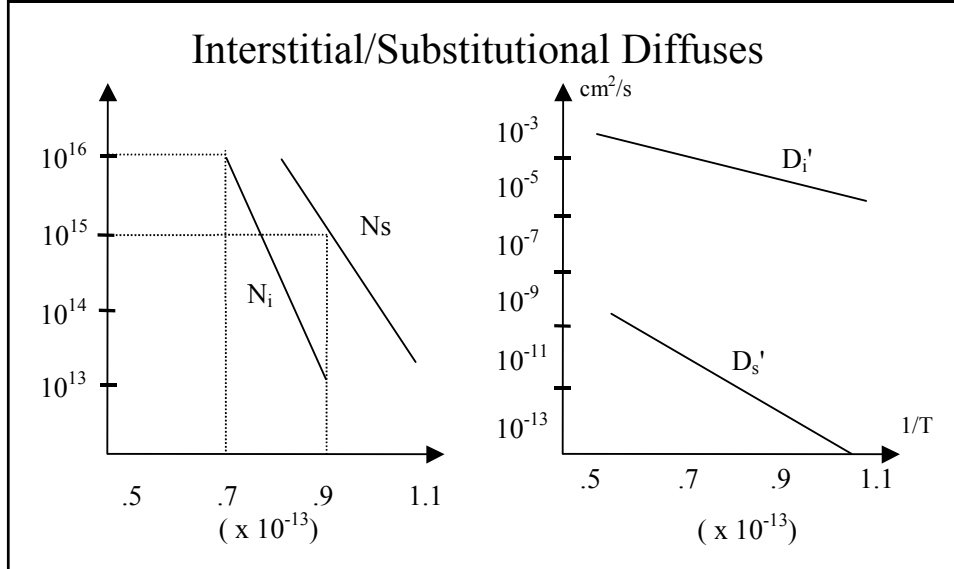
Interaction since:



Dopants

- Group III / V impurities:
 - Substitutional diffusers: B, Al, Ga, In, Sb, As, P
 - (B also interstitial)
- Group I / VIII impurities:
 - Interstitial diffusers H, Na, Li, K, Ar, He
- Transition: substitutional/interstitial:
 - Co, Cu, Au, Fe, Ni, Pt, Ag

Interstit / Substit Diffusers



Fick's First Law of Diffusion

Tetrahedral Si lattice
 Site separation $d = \text{bond length} = \sqrt{3}a / 4$
 Projection on axes $= d / \sqrt{3} = a / 4$

n_1, n_2 impurity atoms in layers 1,2
 Concentrations $N_1 = n_1 / (Ad/\sqrt{3})$, $N_2 = \sqrt{3} n_2 / Ad$
 Atom on boundary P jumps every ν^{-1} sec.
 Net impurity flow across P to right $= \Delta n / \Delta t$
 $= (n_1 / 2 - n_2 / 2) / (\nu^{-1})$
 and $\Delta N / \Delta x = (N_2 - N_1) / (d/\sqrt{3})$

$\therefore \Delta n / \Delta t = (\nu/2)(Ad/\sqrt{3}) (N_1 - N_2)$
 $= - (\nu / 2)(Ad/\sqrt{3}) (d/\sqrt{3}) (\Delta N / \Delta x)$
 $= - A (d^2 \nu / 6) (\Delta N / \Delta x)$

Flux density $j = (\Delta n / \Delta t) / A$,
 Define diffusion constant $D = d^2 \nu / 6$
 $\therefore j = - D (\partial N / \partial x)$ (Fick's First Law)

$D_i = \nu_i d^2 / 6 = (4\nu_o d^2 / 6) \exp -E_m / kT = D_o \exp -E_m / kT$
 $D_s = \nu_s d^2 / 6 = (4\nu_o d^2 / 6) \exp -(E_n + E_s) / kT$
 $= D_o \exp -(E_n + E_s) / kT$

Fick's Second Law of Diffusion

$$\frac{J_1 - J_2}{dx} = \frac{\partial J}{\partial x}$$

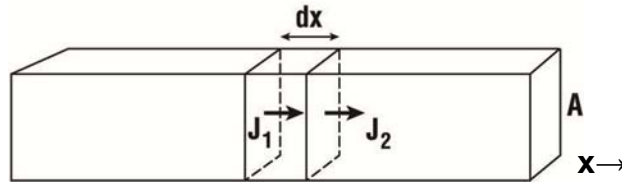


Figure 3.2 A differential volume element in a bar of cross-sectional area A , where J_1 and J_2 are the flux of an impurity into and out of the volume element.

$$\text{In element } \frac{dN}{dt} = A \cdot dx \cdot \frac{\partial C}{\partial t} = -A(J_2 - J_1) = -A \cdot dx \cdot \frac{\partial J}{\partial x}$$

$$\therefore \frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$$

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- Macroscopic dopant redistribution is described by **Fick's first law**, which describes how the flux (or flow) of dopant depends on the doping gradient.

$$F = J = -D \frac{\partial C}{\partial x} \quad (4)$$

- D is the diffusivity ($\text{cm}^2 \text{sec}^{-1}$). D is isotropic in the silicon lattice.
- **Fick's second law** describes how the change in concentration in a volume element is determined by the fluxes in/out of the volume.

$$\frac{\partial C}{\partial t} = -\frac{\partial F}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (5)$$

- If D is a constant this gives

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \rightarrow -D \cdot \nabla^2 C \quad (6)$$

- This is rarely true in practice but this is the only form of Fick's second law which can be solved analytically.

$F_{\text{in}} \rightarrow J_1$ $F_{\text{out}} \rightarrow J_2$

ΔC $c/s \text{ area } A$

Δx

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Analytic Solutions Of Fick's Laws

1. **Limited Source:** Consider a fixed dose Q , introduced as a delta function at the origin.

- The solution that satisfies Fick's second law is

$$C(x,t) = \frac{Q}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (7)$$

- Important consequences:
 - Dose Q remains constant
 - Peak concentration decreases as $1/\sqrt{t}$
 - Diffusion distance increases as $2\sqrt{Dt}$

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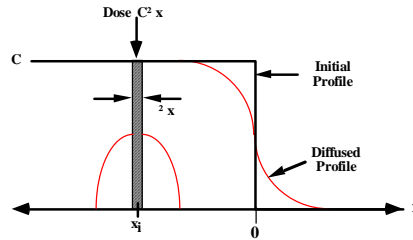
2. **Constant Source Near A Surface:**

- This is similar to the previous case except the diffusion only goes in one direction.

$$C(x,t) = \frac{Q}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) = C(0,t) \exp\left(-\frac{x^2}{4Dt}\right) \quad (8)$$

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3. Infinite Source:



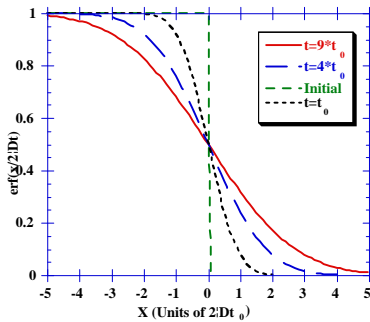
- The infinite source is made up of small slices each diffusing as a Gaussian.

$$\begin{aligned}
 C(x,t) &= \frac{C}{2\sqrt{\pi Dt}} \sum_{i=1}^n \Delta x_i \exp\left(-\frac{(x-x_i)^2}{4Dt}\right) \quad (9) \\
 &= \frac{C}{2\sqrt{\pi Dt}} \int_0^\infty \exp\left(-\frac{(x-\alpha)^2}{4Dt}\right) d\alpha = \frac{C}{\sqrt{\pi}} \int_{-\infty}^{x/2\sqrt{Dt}} \exp(-\eta^2) d\eta \text{ where } \eta = \frac{x-\alpha}{2\sqrt{Dt}} \\
 &= \frac{C}{2} \left(1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right) \text{ where } \operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\eta^2) d\eta \\
 &= \frac{C}{2} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)
 \end{aligned}$$

- The solution which satisfies Fick's second law is

$$C(x,t) = \frac{C}{2} \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \right] = C_s \left[\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \right] \quad (10)$$

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- Important consequences of error function solution:

- Symmetry about mid-point allows solution for constant surface concentration to be derived.
- Error function solution is made up of a sum of Gaussian delta function solutions.
- Dose beyond $x = 0$ continues to increase with annealing time.

(See text Appendix Plummer/Ag or Campbell/V for properties of erfc.)

4. Constant Surface Concentration:

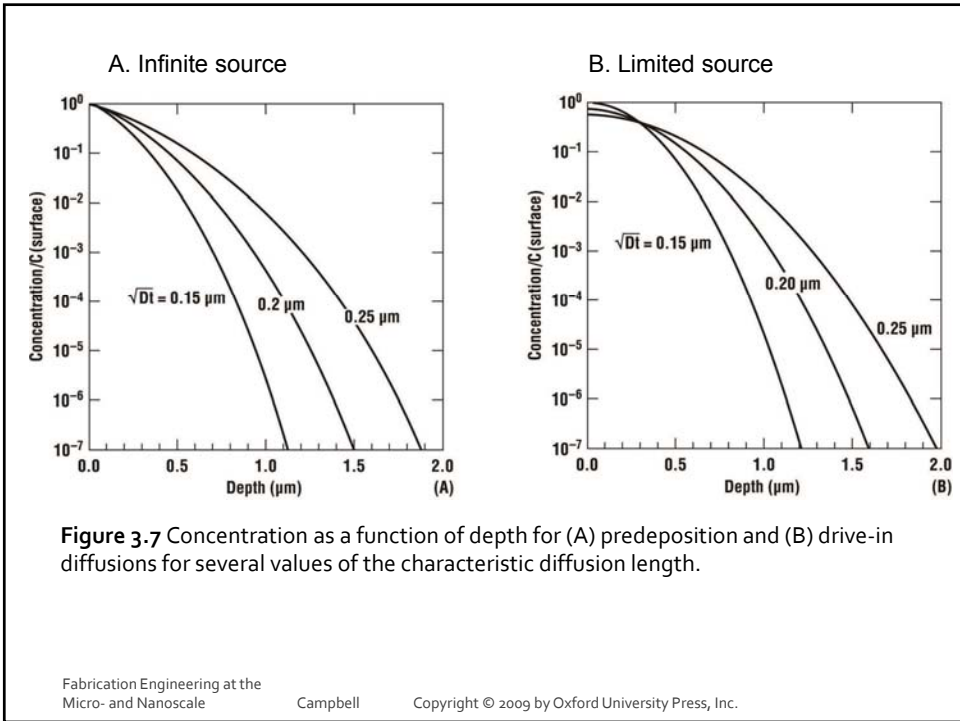
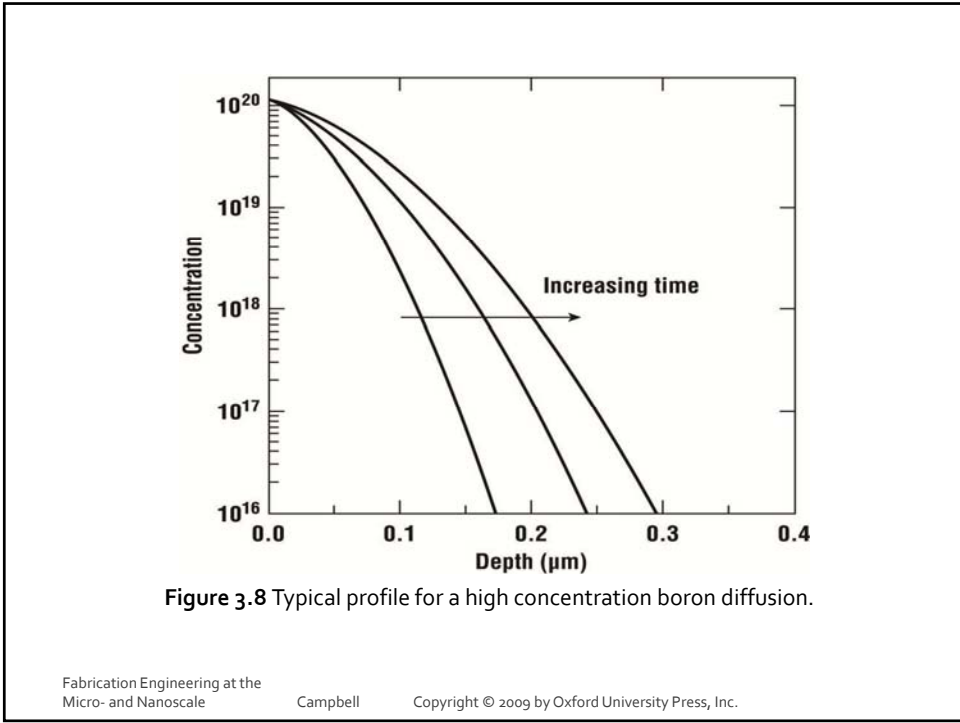
- Just the right hand side of the above figure.

$$C(x,t) = C_s \left[\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \right] \quad (11)$$

- Note that the total dose is given by

$$Q = \int_0^\infty C_s \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \right] dx = \frac{2C_s}{\sqrt{\pi}} \sqrt{Dt} \quad (12)$$

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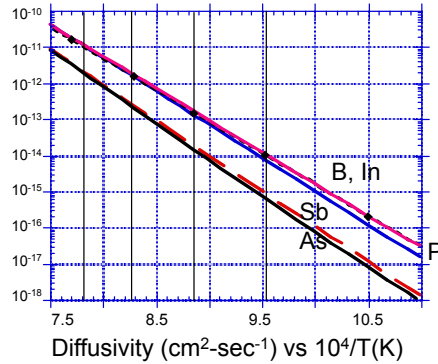


Intrinsic Dopant Diffusion Coefficients

- Intrinsic dopant diffusion coefficients are found to be of the form:

$$D = D^0 \exp\left(\frac{-E_A}{kT}\right) \quad (13)$$

	Si	B	In	As	Sb	P	Units
D^0	560	1.0	1.2	9.17	4.58	4.70	$\text{cm}^2 \text{sec}^{-1}$
E_A	4.76	3.5	3.5	3.99	3.88	3.68	eV



- Note that n_i is very large at process temperatures, so "intrinsic" actually applies under many conditions.
- Note the "slow" and "fast" diffusers. Solubility is also an issue in choosing a particular dopant.

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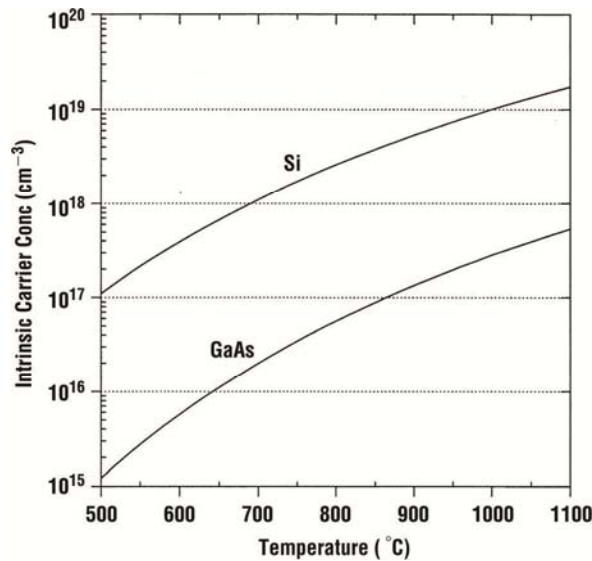


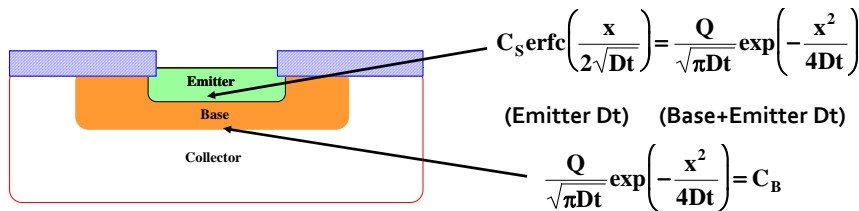
Figure 3.4 Intrinsic carrier concentration of silicon and GaAs as a function of temperature.

Effect Of Successive Diffusions

- If a dopant is diffused at temperature T_1 for time t_1 and then is diffused at temperature T_2 for time t_2 , the total effective Dt is given by the sum of all the individual Dt products.

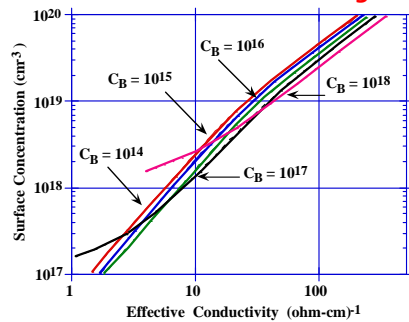
$$Dt_{\text{eff}} = \sum Dt = D_1 t_1 + D_2 t_2 + \dots \quad (14)$$

- The Gaussian solution only holds if the Dt used to introduce the dopant is small compared with the final Dt for the drive-in; i.e. if an initial delta function approximation is reasonable.
- Example: In a bipolar transistor, if the emitter profile is formed by a predep and the base profile by an implant + drive-in, then the junctions occur where:

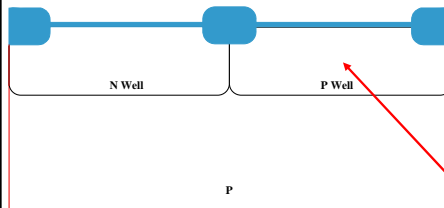


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Design Of Diffused Layers



- Eqn. (3) has been numerically integrated for specific cases (erfc and Gaussian).
- Example of Irvin's curves, in this case for P type Gaussian profiles.



- We can now consider how to design a boron diffusion process (say for the well or tub of a CMOS process, such that:

$$\left. \begin{aligned} \rho_s &= 900 \Omega / \text{square} \\ x_j &= 3 \mu\text{m} \\ C_{BC} &= 1 \times 10^{15} \text{ cm}^{-3} \text{ (substrate concentration)} \end{aligned} \right\}$$

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- The average conductivity of the layer is $\bar{\sigma} = \frac{1}{\rho_s x_j} = \frac{1}{(900 \Omega / \text{sq})(3 \times 10^{-4} \text{ cm})} = 3.7 (\Omega \cdot \text{cm})^{-1}$
- From Irvin's curve we obtain $C_s \approx 4 \times 10^{17} / \text{cm}^3$
- We can surmise that the profile is Gaussian after drive-in. $\therefore C_{BC} = \frac{Q}{\sqrt{\pi Dt}} \exp\left(-\frac{x_j^2}{4Dt}\right) = C_s \exp\left(-\frac{x_j^2}{4Dt}\right)$

so that

$$Dt = \frac{x_j^2}{4 \ln \frac{C_s}{C_{bc}}} = \frac{(3 \times 10^{-4})^2}{4 \ln \left(\frac{4 \times 10^{17}}{10^{15}}\right)} = 3.7 \times 10^{-9} \text{ cm}^2$$

- If the drive-in is done at 1100 °C, then the boron diffusivity is $D = 1.5 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$
- The drive-in time is therefore $t_{\text{drive-in}} = \frac{3.7 \times 10^{-9} \text{ cm}^2}{1.5 \times 10^{-13} \text{ cm}^2 / \text{sec}} = 6.8 \text{ hours}$

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- Given both the surface concentration and Dt, the initial dose can be calculated for this Gaussian profile. $Q = C_s \sqrt{\pi Dt} = (4 \times 10^{17}) (\sqrt{\pi}) (\sqrt{3.7 \times 10^{-9}}) = 4.3 \times 10^{13} \text{ cm}^{-2}$
- This dose could easily be implanted in a narrow layer close to the surface, justifying the implicit assumption in the Gaussian profile that the initial distribution approximates a delta function.

- If a gas/solid phase pre-deposition step at 950 °C were used, i.e. infinite source, then $\left\{ \begin{array}{l} \text{B solid solubility at } 950 \text{ }^\circ\text{C is } 2.5 \times 10^{20} \text{ cm}^{-3} \\ \text{B diffusivity is } 4.2 \times 10^{-15} \text{ cm}^2 \text{ sec}^{-1} \end{array} \right.$
- The dose for an erfc profile is $Q = \frac{2C_s}{\sqrt{\pi}} \sqrt{Dt}$
- So that the time required for the predeposition is $t_{\text{pre-dep}} = \left(\frac{4.3 \times 10^{13}}{2.5 \times 10^{20}}\right)^2 \left(\frac{\sqrt{\pi}}{2}\right)^2 \frac{1}{4.2 \times 10^{-15}} = 5.5 \text{ sec}$

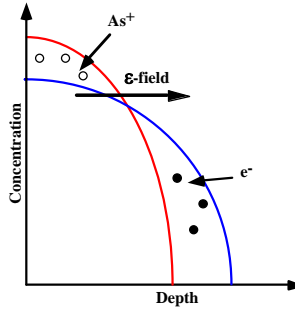
Check delta function approximation:

$$Dt_{\text{predep}} = 5.5 \times 4.2 \times 10^{-15} = 2.3 \times 10^{-14} \ll Dt_{\text{drive-in}} = 3.7 \times 10^{-9}$$

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Modifications Of Fick's Laws

A. Electric Field Effects

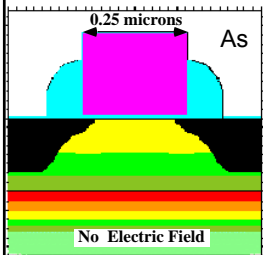


The graph shows concentration on the y-axis and depth on the x-axis. Two curves are shown: a red curve for As⁺ and a blue curve for e⁻. An arrow labeled 'E-field' points to the right. The As⁺ curve starts at a high concentration at the surface and decays with depth. The e⁻ curve starts at a lower concentration and decays more rapidly.

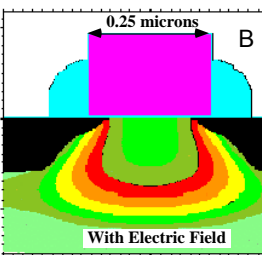
- When the doping is higher than n_i , ϵ field effects become important.
- ϵ field induced by higher mobility of electrons and holes compared with dopant ions.
- ϵ field enhances the diffusion of dopants causing the field (see derivation in text).

$$J = -hD_A \frac{\partial C}{\partial x} \quad (16)$$

where $h = 1 + \frac{C}{\sqrt{C^2 + 4n_i^2}} \quad (17)$ (See next slide)



0.25 microns As
No Electric Field



0.25 microns B
With Electric Field

- SUPREM simulation at 1000°C. Note the boron profile ($h \leq 2$ for the As but ϵ field effects dominate the B diffusion).
- Field effects can dominate the doping distribution near the source/drain of a MOS device.

As electric field pulls low density B back into the n+ region, it depletes B at the junction

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Total flux $F = -D \frac{\partial C}{\partial x} + Cv$ where $v =$ velocity in electric field ϵ

$$\therefore \frac{\partial C}{\partial t} = -\frac{\partial F}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) - v \frac{\partial C}{\partial x},$$

or using

$$v = \mu \epsilon = \frac{q}{kT} D \frac{\partial \phi}{\partial x} = \frac{q}{kT} D \frac{\partial}{\partial x} \left[-\frac{kT}{q} \ln \frac{n}{n_i} \right] = D \frac{\partial}{\partial x} \left[\ln \frac{n}{n_i} \right]$$

$$F = -D \frac{\partial C}{\partial x} + DC \frac{\partial}{\partial x} \ln \frac{n}{n_i} = -DC \left[\frac{1}{C} \frac{\partial C}{\partial x} + \frac{\partial}{\partial x} \ln \frac{n}{n_i} \right]$$

$$= -DC \left[\frac{\partial}{\partial x} \ln C + \frac{\partial}{\partial x} \ln \frac{n}{n_i} \right] = -DC \frac{\partial}{\partial x} \left(\ln \frac{n}{n_i} C \right)$$

or using $N_D + p \approx N_A + n$
 $np = n_i^2$ and $C = |N_D - N_A|$

get $n = C + \frac{n_i^2}{n}$, i.e. $n^2 - Cn - n_i^2 = 0$,

giving $n = \frac{C \pm \sqrt{C^2 + 4n_i^2}}{2}$ and $2n \frac{dn}{dx} - C \frac{dn}{dx} - n \frac{dC}{dx} = 0$

i.e. $\frac{dn}{dx} = \frac{n \frac{dC}{dx}}{2n - C} = \frac{n \frac{dC}{dx}}{\sqrt{C^2 + 4n_i^2}}$

$$\text{gives } \frac{\partial}{\partial x} \ln \frac{n}{n_i} = \frac{n_i}{n} \frac{1}{n_i} \frac{\partial n}{\partial x} = \frac{\partial C}{\partial x} \frac{1}{\sqrt{C^2 + 4n_i^2}}$$

and $F = J = -D \frac{\partial C}{\partial x} - DC \frac{\partial}{\partial x} \ln \frac{n}{n_i}$

$$= -D \frac{\partial C}{\partial x} - DC \frac{\partial C}{\partial x} \frac{1}{\sqrt{C^2 + 4n_i^2}}$$

$$= -D \left[1 + \frac{C}{\sqrt{C^2 + 4n_i^2}} \right] \frac{\partial C}{\partial x}$$

$$= -hD \frac{\partial C}{\partial x}$$

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Electric Field Assist

Ionized impurities driven by field AND conc'n gradient

Field ϵ generated by diffusion process at high doping levels $N \gg n_i$

- i.e. effect increases at high N or low T

N.type impurity --> donor ion + electron (e^-)

- electrons diffuse rapidly (out-run ions)
- creates space charge and field
- field enhances ion diffusion, i.e. increases D

1. For N-type:

$$J = -D \frac{\partial N}{\partial x} + (\mu N \epsilon)$$

Einstein relation for electrons $\epsilon = - (kT/q)(1/n)dn/dx$

Substitute $D = (kT/q) \mu$ for ions

$$J = -D \frac{\partial N}{\partial x} - (q/kT) D N \cdot (kT/q) n^{-1} dn/dx$$

$$= -D \frac{dN}{dx} - D (N/n) \frac{dn}{dx}$$

$$= -D (1 + \frac{dn}{dN}) \frac{dN}{dx} \text{ for } n \approx N$$

$$\therefore D_{\text{eff}} = D (1 + \frac{dn}{dN}) \rightarrow 2D$$

2. (N-type still)

$$n = (N_D / 2) + [(N_D / 2)^2 + n_i^2]^{1/2}$$

$$\frac{dn}{dN_D} = \frac{1}{2} + \frac{1}{2} [(N_D / 2)^2 + n_i^2]^{-1/2} 2(N_D / 2) / 2$$

$$= \frac{1}{2} \{ 1 + [1 + (2n_i / N_D)^2]^{-1/2} \}$$

$$\rightarrow \text{max } 1 \text{ as } n_i / N_D \rightarrow 0$$

$$\therefore D_{\text{eff}} \rightarrow 2D$$

Charged Defects #1

Substitutional diffusion

Impurity ion / vacancy interaction

Vacancies have associated charge state

Represent as $V^+, V^0, V^-, V^{2-}, 3^-, \text{etc...}$

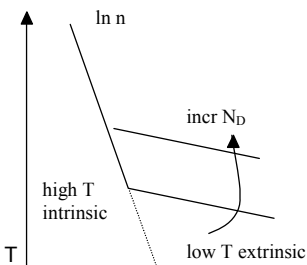
Diffusion due to various vacancies

$$D_i^+, D_i^0, D_i^-, D_i^{2-}, D_i^{3-}, \text{ etc...}$$

□ Intrinsic diffusivity: $D_i = D_i^+ + D_i^0 + D_i^- + D_i^{2-} + \dots$

↑conventional

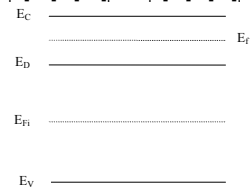
Extrinsic Diffusivity



High doping, low T

E_F shifts, defect concentrations change

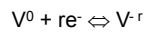
$$D = D_i^+ [V^+] / [V^+]_i + D_i^0 [V^0] / [V^0]_i + D_i^- [V^-] / [V^-]_i + \dots$$



Charged Defects #2

$[V^0] = [V^0]_i$ not charge dependent
 $V^0 + h^+ \leftrightarrow V^+$ (h^+ = hole)
 $\therefore k_1 = [V^+] / p [V^0] = [V^+] / p [V^0]_i$
 & for the intrinsic case:
 $k_1 = [V^+]_i / n_i [V^0]_i \therefore [V^+] / [V^+]_i = p / n_i$

Generalize for V^{-r}



$K_r = [V^{-r}] / n^r [V^0] = [V^{-r}]_i / n_i^r [V^0]_i$

$[V^{-r}] / [V^{-r}]_i = (n / n_i)^r$

$\therefore D = D_i^+ (p/n_i) + D_i^0 + D_i^- (n/n_i) + D_i^{2-} (n/n_i)^2 + \dots$

$D_{eff} = [D_i^+ (p/n_i) + D_i^0 + D_i^- (n/n_i) + \dots] h$

where field enhancement $h = 1 + [1 + (2n_i / N)^2]^{-1/2}$

N type impurity diffusion:

$D_i^- D_i^{2-}, \dots$ dominant

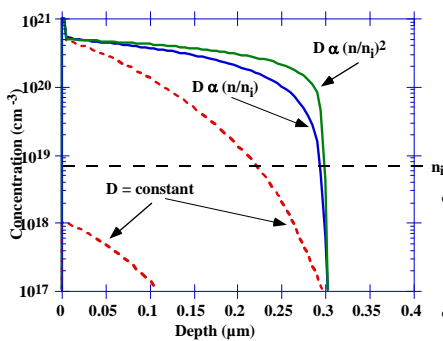
P type impurity diffusion:

D_i^+ dominant

GaAs vacancies neutral:

$D_i \approx hD_i^0$

B. Concentration Dependent Diffusivity



• At high doping concentrations, the diffusivity appears to increase. Fick's equation must then be solved numerically since $D \neq \text{constant}$.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D_A^{eff} \frac{\partial C}{\partial x} \right) \tag{5}$$

• Isoconcentration experiments indicate the dependence of D on concentration; e.g. isotopes B^{10} in a B^{11} background.

• Often, D is well described by

$$D_A^{eff} = D^0 + D^- \left(\frac{n}{n_i} \right) + D^- \left(\frac{n}{n_i} \right)^2 \text{ for n - type, and} \tag{18}$$

$$D_A^{eff} = D^0 + D^+ \left(\frac{p}{n_i} \right) + D^{++} \left(\frac{p}{n_i} \right)^2 \text{ for p - type}$$

• The n and n^2 (p and p^2 for P type dopants) terms are due to charged defect diffusion mechanisms.

For intrinsic ($n = p = n_i$):

$$D_A^* = D_0 + D^- + D^=$$

and

$$D_A^{eff} = D_A^* \left[\frac{1 + \beta \frac{n}{n_i} + \gamma \left(\frac{n}{n_i} \right)^2}{1 + \beta + \gamma} \right]$$

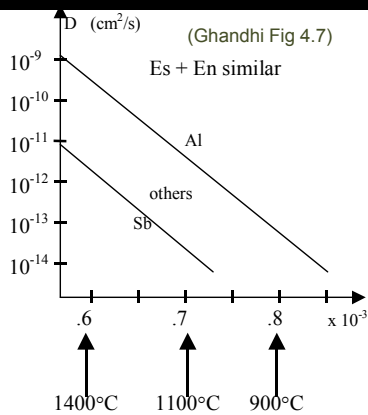
where $\beta = \frac{D^-}{D_0}$ and $\gamma = \frac{D^=}{D_0}$

$$D = D_0 \exp\left(-\frac{D.E}{kT}\right) \quad (19)$$

	Si	B	In	As	Sb	P
$D^0 \text{ cm}^2\text{sec}^{-1}$	560	0.05	0.6	0.011	0.214	3.85
$D^0.E \text{ eV}$	4.76	3.5	3.5	3.44	3.65	3.66
$D^+ \text{ cm}^2\text{sec}^{-1}$		0.95	0.6			
$D^+.E \text{ eV}$		3.5	3.5			
$D^- \text{ cm}^2\text{sec}^{-1}$				31.0	15.0	4.44
$D^-.E \text{ eV}$				4.15	4.08	4.0
$D^= \text{ cm}^2\text{sec}^{-1}$						44.2
$D^=.E \text{ eV}$						4.37

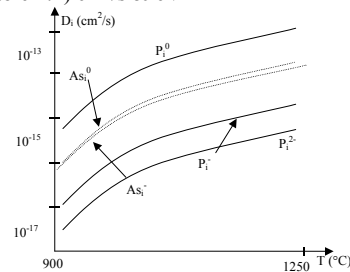
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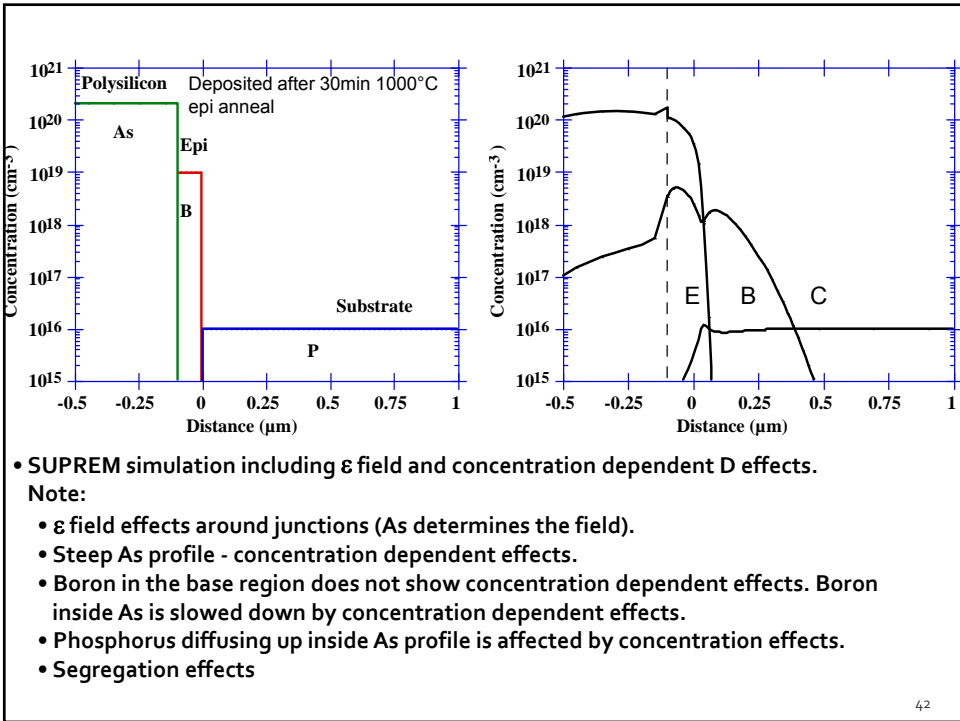
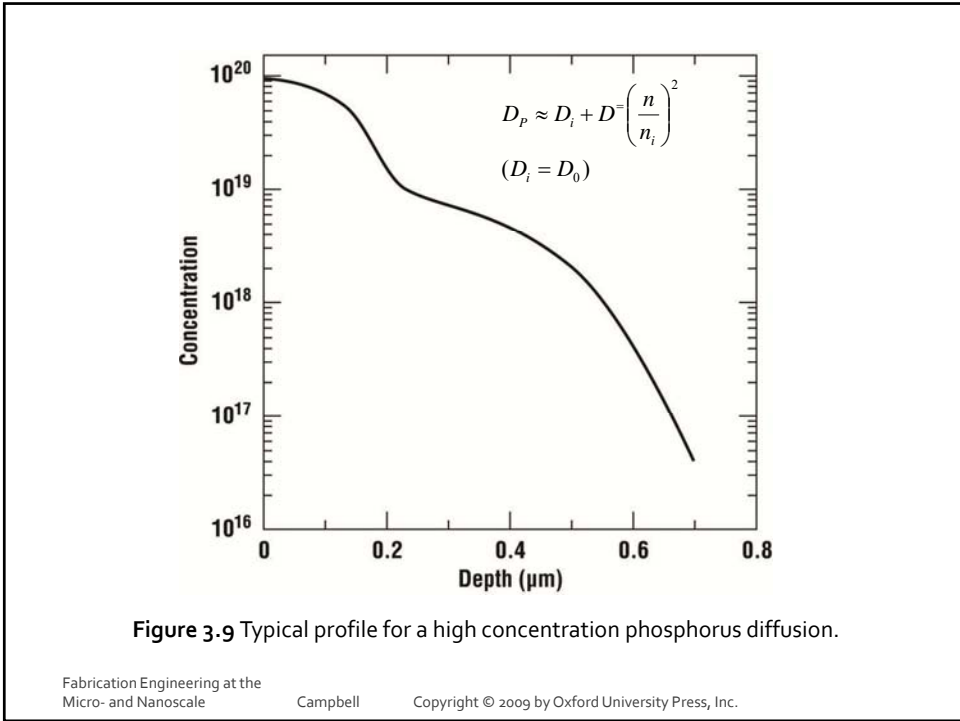
Substitutional Diffusers



		P	As	Sb	B	Al	Ga
D_i^0	D_0	3.85	0.066	0.214	0.037	1.385	0.374
	E_0	3.66	3.44	3.65	3.46	3.41	3.39
D_i^+	D_0				0.76	2480	28.5
	E_0				3.46	4.2	3.92
D_i^-	D_0	4.44	22.9	13			
	E_0	4	4.1	4			
D_i^{2-}	D_0	44.2					
	E_0	4.37					

(Ghandhi Table 4.1) cm^2/s & eV





C. Segregation

- Dopants segregate at interfaces. Recall from Lecture 2,
- This gives an interface flux of

$$F = k_1 C_A - k_2 C_B = 0 \text{ in equilibrium}$$

$$\therefore k_O = \frac{C_B}{C_A} = \frac{k_1}{k_2} \quad (20)$$

$$F = k_1 \left(C_A - \frac{C_B}{k_O} \right) \quad (21)$$

Oxidation of a uniformly doped boron substrate depletes the boron into the growing SiO₂ (SUPREM simulation).

$$k_0 = \frac{C_{Si}}{C_{SiO_2}} = 0.3 \text{ (B) \& 10 (As, Sb, \& P)}$$

N-type dopants tend to pile-up while boron depletes (SUPREM simulation).

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D. Interfacial Dopant Pile-up

- Dopants may also segregate to an interface layer, perhaps only a monolayer thick. Interfacial dopant dose loss or pile-up may consume up to 50% of the dose in a shallow layer.

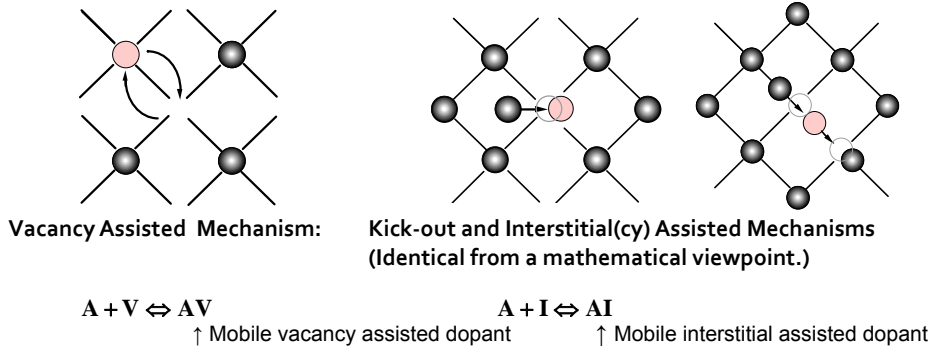
In the experiment (right) 40% of the dose was lost in a 30 sec anneal.

Kasnavi et. al.

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Atomic Scale Diffusion

- Fick's first law macroscopically describes dopant diffusion at low concentrations.
 - "Fixes" to this law to account for experimental observations (concentration dependent diffusion and ϵ field effects), are useful, but at this point the complexity of the "fixes" begins to outweigh their usefulness.
 - Many effects (OED, TED etc) that are very important experimentally, cannot be explained by the macroscopic models discussed so far.
- \therefore We turn to an atomistic view of diffusion for a deeper understanding.



OED: oxidation enhanced diffusion; TED: transient enhanced diffusion

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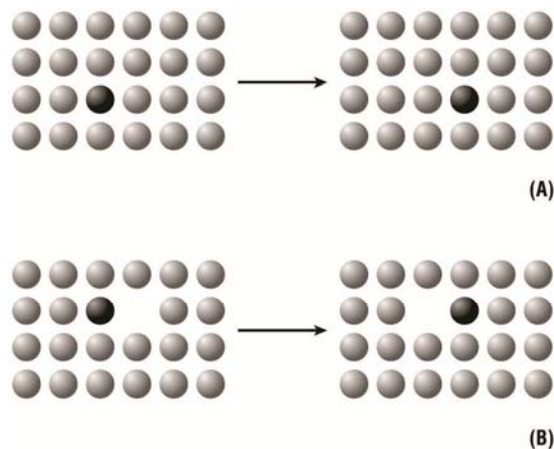


Figure 3.3 Diffusion of an impurity atom by direct exchange (A) and by vacancy exchange (B). The latter is much more likely owing to the lower energy required.

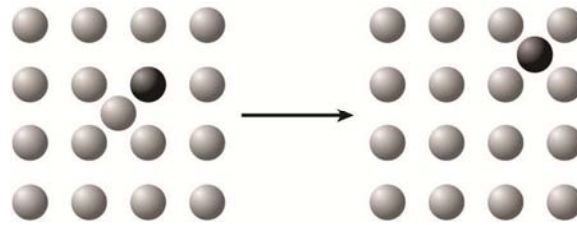


Figure 3.5 In interstitialcy diffusion, an interstitial silicon atom displaces a substitutional impurity, driving it to an interstitial site, where it diffuses some distance before it returns to a substitutional site.

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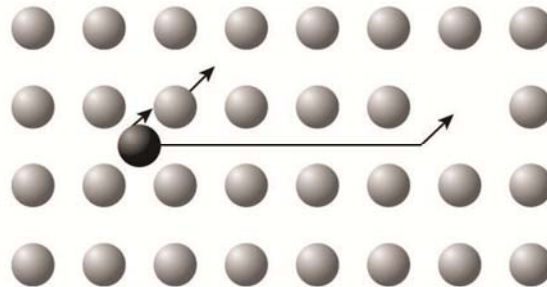


Figure 3.6 The kick-out (left) and Frank–Turnbull mechanisms (right).

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A. Modeling I And V Components Of Diffusion

- Oxidation provides an I injection source.
- Nitridation provides a V injection source.
- Stacking faults serve as "detectors" as do dopants which diffuse.
- Experiments like these have "proven" that both point defects are important in silicon. Therefore,

$$D_A^{eff} = D_A^* \left(f_I \frac{C_I}{C_I^*} + f_V \frac{C_V}{C_V^*} \right) \quad (22)$$

D_A^*, C_I^*, C_V^* equilibrium values

- Thus dopant diffusion can be enhanced or retarded by changes in the point defect concentrations. ($f_I + f_V = 1$)

	f_I	f_V
Silicon	0.6	0.4
Boron	1.0	0
Phosphorus	1.0	0
Arsenic	0.4	0.6
Antimony	0.02	0.98

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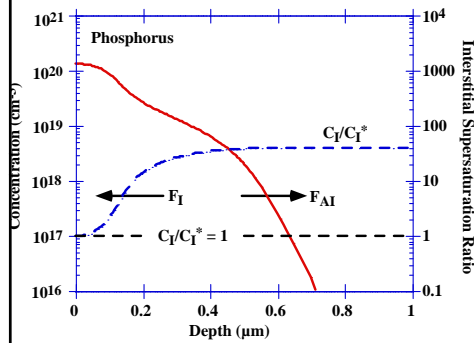
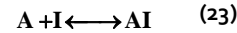
- Measurements of enhanced or retarded diffusion under oxidizing or nitriding conditions allow an estimate of the I or V component of diffusion to be made.
- Oxidation injects interstitials, raises C_I / C_I^* and reduces C_V / C_V^* through I-V recombination in the bulk silicon. Nitridation does exactly the opposite.

- TSUPREM IV simulations of oxidation enhanced diffusion of boron (OED) and oxidation retarded diffusion of antimony (ORD) during the growth of a thermal oxide on the surface of silicon. The two shallow profiles are antimony, the two deeper profiles are boron.
- Note that the C_I / C_I^* and C_V / C_V^* profiles are relatively flat indicating the "stiff source" characteristic of the oxidation process.

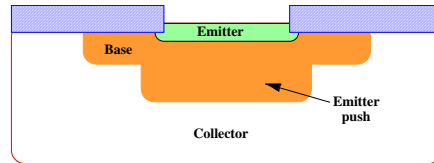
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B. Modeling Atomic Scale Reactions

- Consider the simple chemical reaction
- This contains a surprising amount of physics.
- For example OED is explained because oxidation injects I driving the equation to the right, creating more A-I pairs and enhancing the dopant D.



Phosphorus diffuses with I, and releases them in the bulk. This enhances the tail region D.



"Emitter push" is also explained by this mechanism.

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- If we assume "chemical equilibrium" between dopants and defects in Eqn. (23), then from the law of mass action,

$$C_{AI} = k C_A C_I \quad (24)$$

- Applying Fick's law to the mobile species

$$F_{AI} = -d_{AI} \frac{\partial C_{AI}}{\partial x} \quad (25)$$

- Applying the chain rule from calculus,

$$F_{AI} = -d_{AI} \left(k C_I \frac{\partial C_A}{\partial x} + k C_A \frac{\partial C_I}{\partial x} \right) \quad (26)$$

- Thus, gradients in defects as well as gradients in dopant concentrations can drive diffusion fluxes.

- The overall flux equation solved by simulators like SUPREM is

$$F_{BI}^{tot} = D_{BI}^* \cdot \left(\frac{1 + \beta \frac{p}{n_i}}{1 + \beta} \right) \cdot \frac{C_{I^o}}{C_{I^o}^*} \cdot C_{B^-} \cdot \frac{\partial}{\partial x} \ln \left(C_{B^-} \frac{C_{I^o}}{C_{I^o}^*} \frac{p}{n_i} \right) \quad (27)$$

(written for boron diffusing with neutral and positive interstitials as an example).

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$$F_{BI}^{tot} = D_{BI}^* \cdot \left(\frac{1 + \beta \frac{p}{n_i}}{1 + \beta} \right) \cdot \frac{C_{I^0}}{C_{I^0}^*} \cdot C_B^- \cdot \frac{\partial}{\partial x} \ln \left(C_B^- \frac{C_{I^0}}{C_{I^0}^*} \frac{p}{n_i} \right) \quad (27)$$

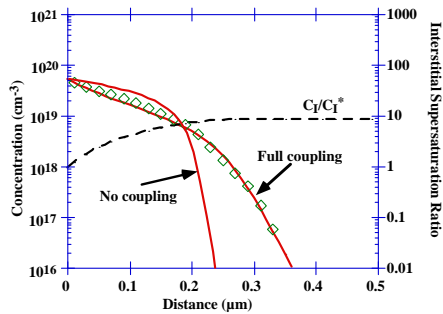
• Thus there are several distinct effects that drive the dopant diffusion:

- inert, low concentration diffusion, driven by the dopant gradient (D_{BI}^*)
- the interstitial supersaturation $C_{I^0} / C_{I^0}^*$
- high concentration effects on the dopant diffusivity $\left(\frac{1 + \beta \frac{p}{n_i}}{1 + \beta} \right)$
- the electric field effect $\frac{\partial \ln p}{\partial x \cdot n_i}$

• Compare the above expression with Fick's Law, which is where we started.

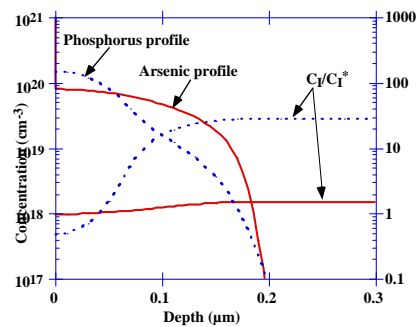
$$F = -D \frac{\partial C}{\partial x} \quad (4)$$

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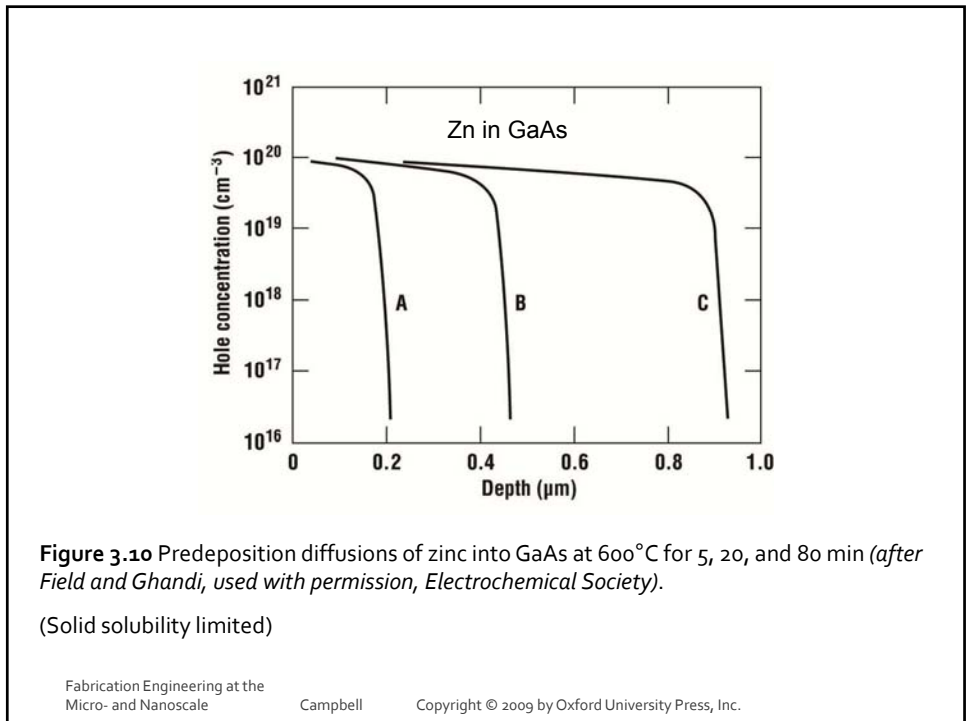
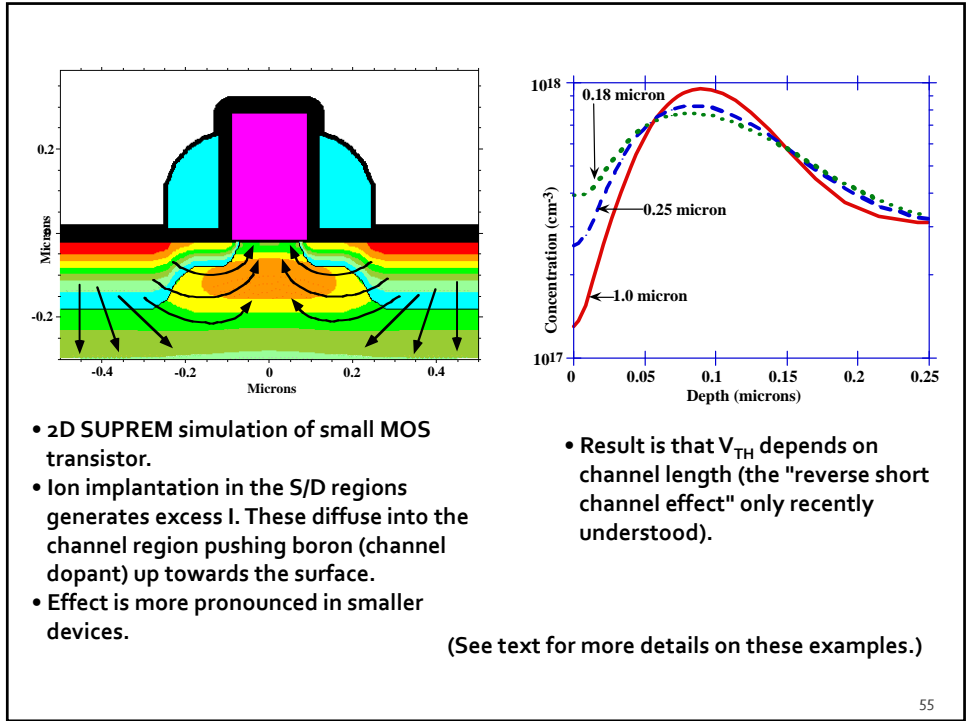
• TSUPREM IV simulations of boron diffused from a polysilicon source for 8 hours at 850 °C, with experimental data (diamonds) from [7.29]. The simulations use identical coefficients, but with and without full coupling between dopants and defects. The C_I / C_I^* curve (right axis) is for the fully coupled case. Without full coupling, $C_I / C_I^* = 1$.

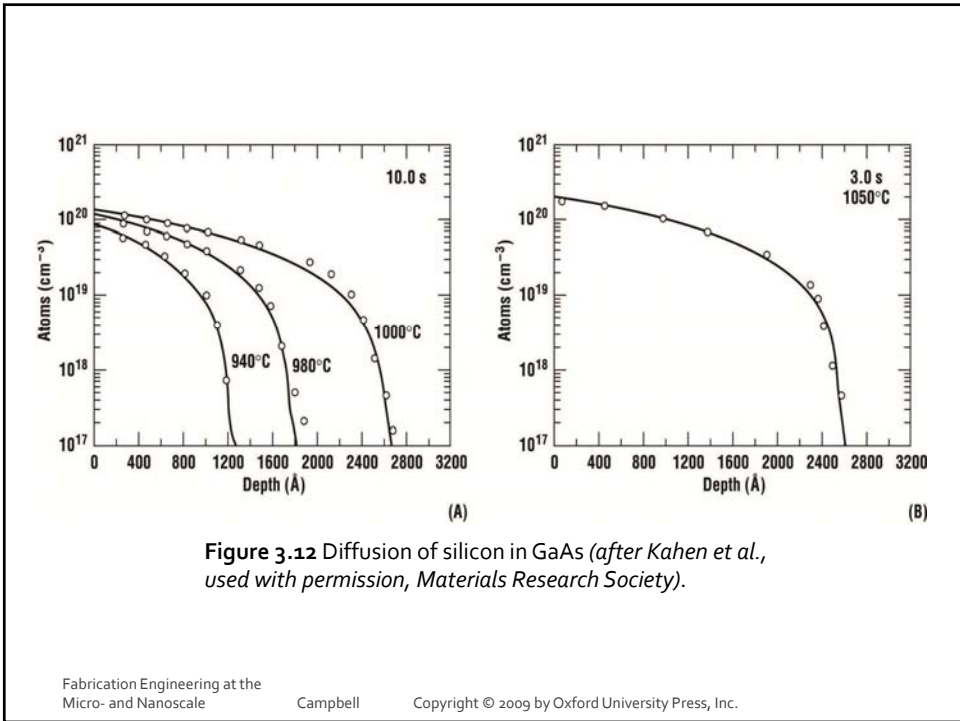
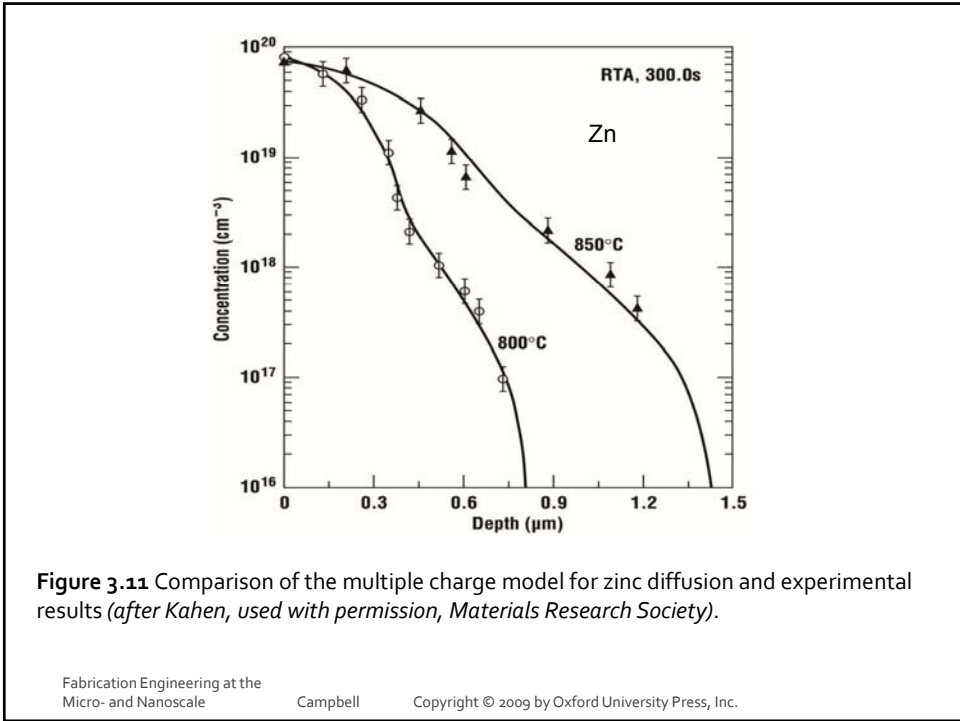
• No coupling produces a “boxier” profile because of concentration dependent diffusion.

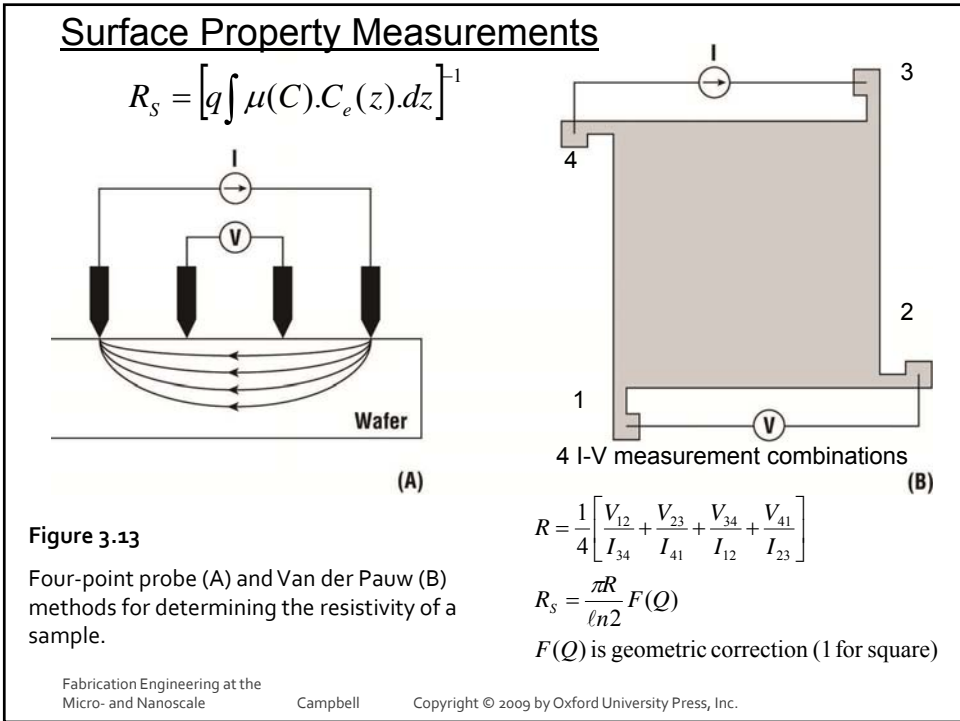
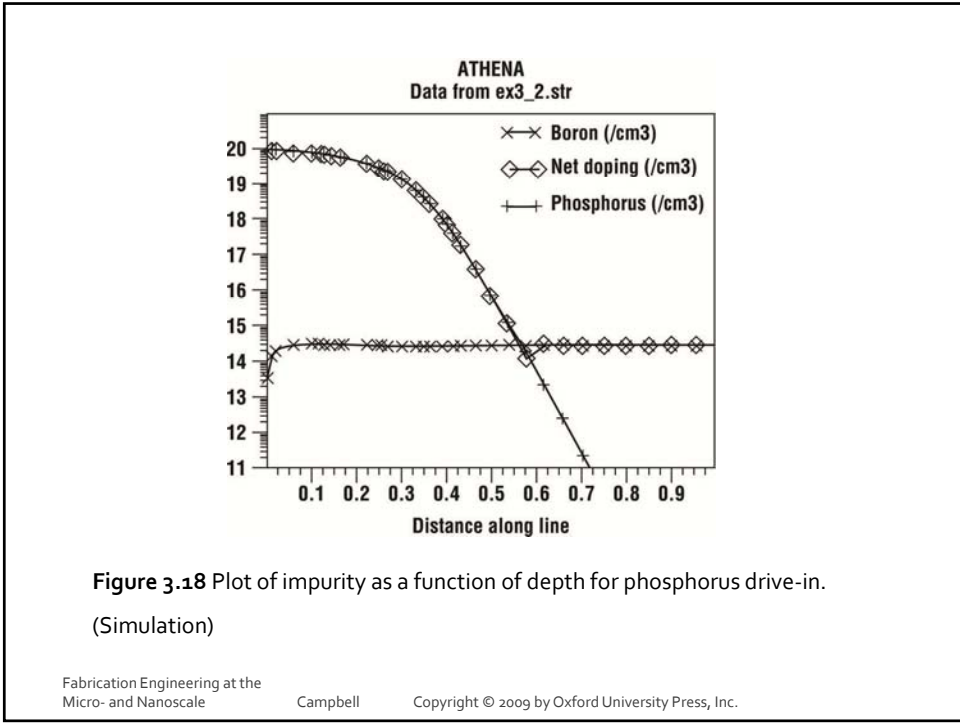


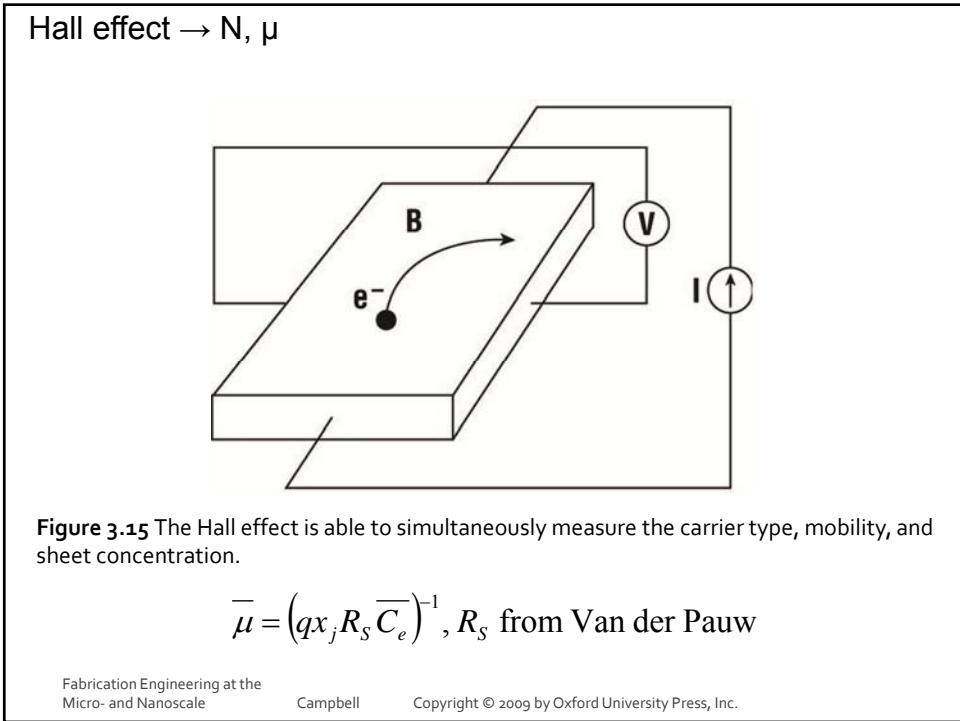
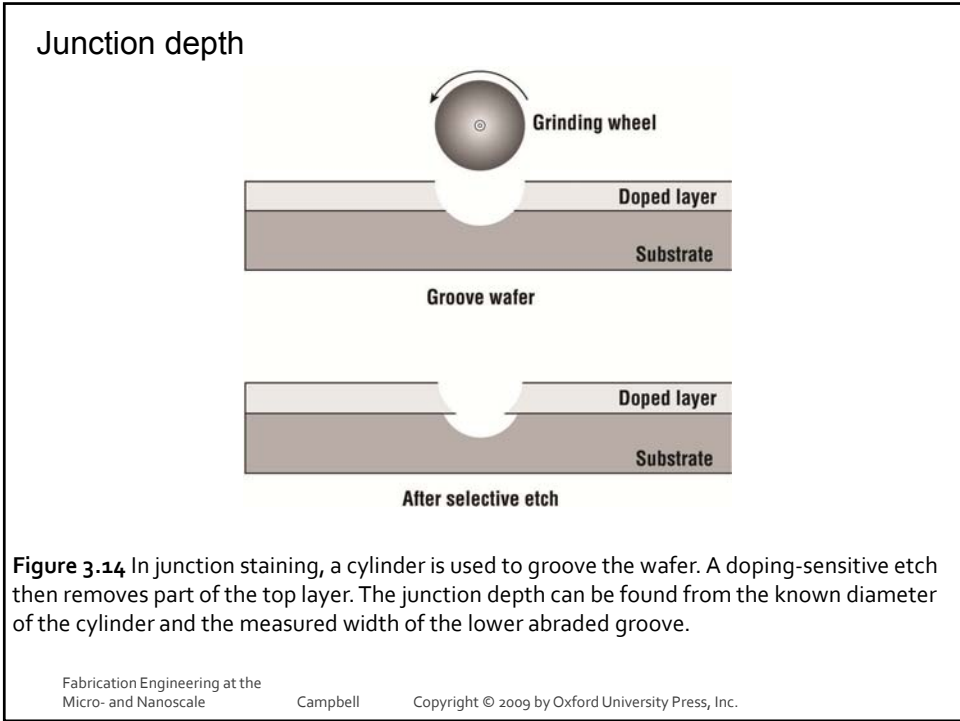
• TSUPREM IV simulations of the interstitial supersaturations generated by a phosphorus versus an arsenic diffusion to the same depth. The fast diffusing phosphorus profile has a larger effect on C_I / C_I^* than the slow diffusing arsenic profile.

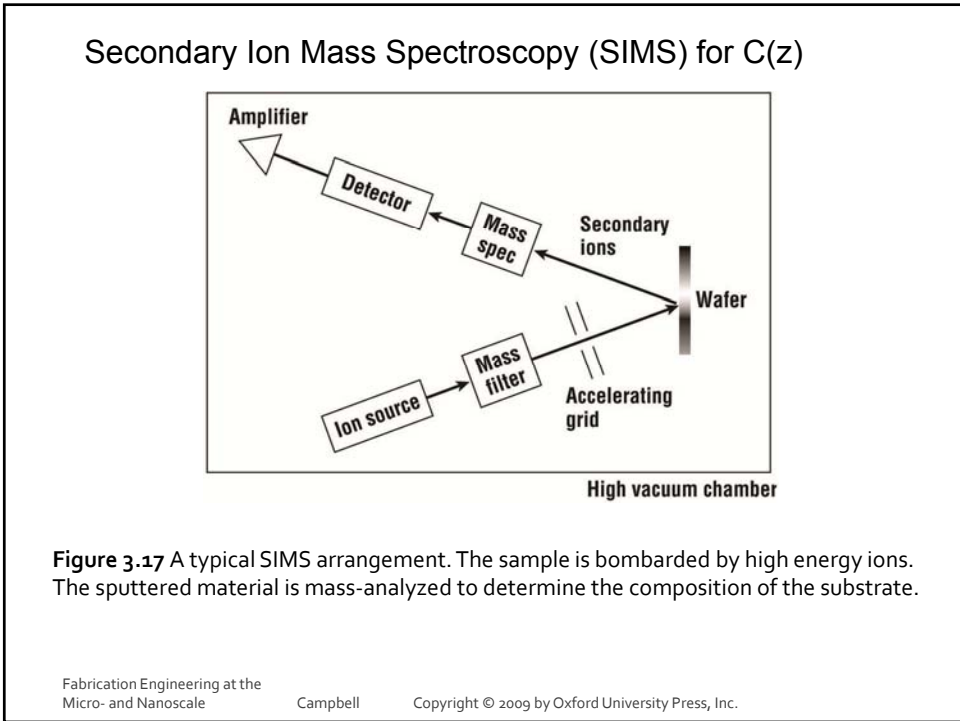
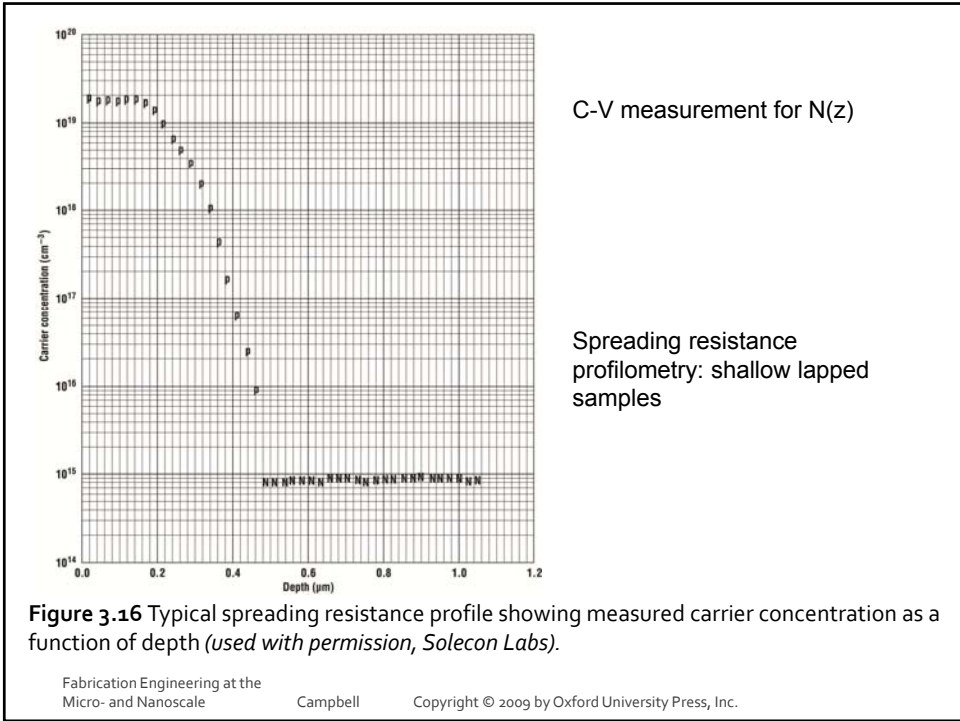
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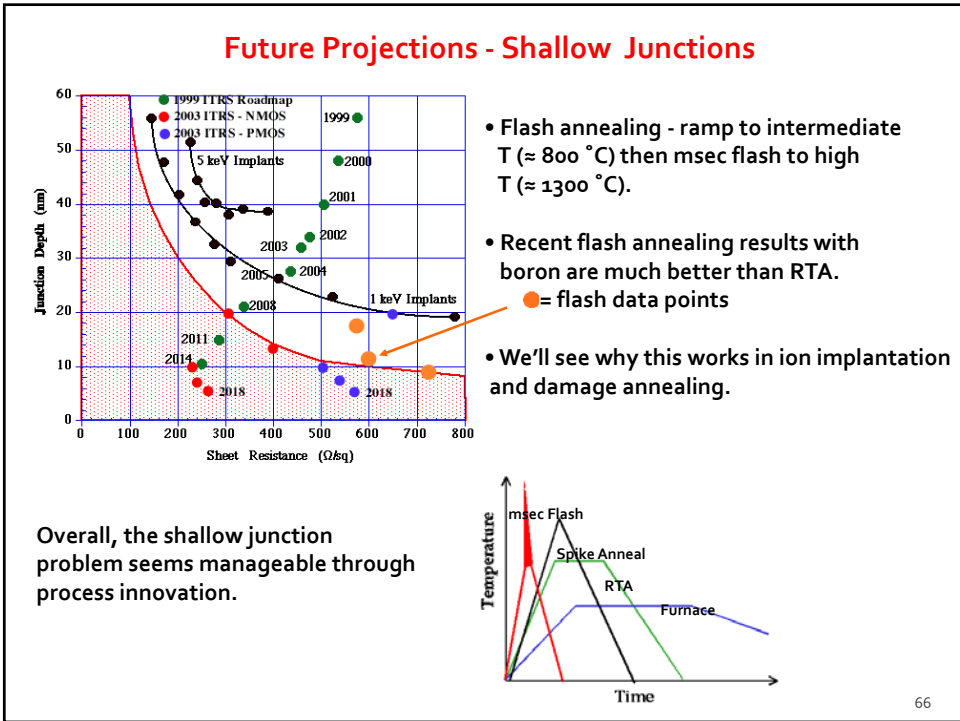
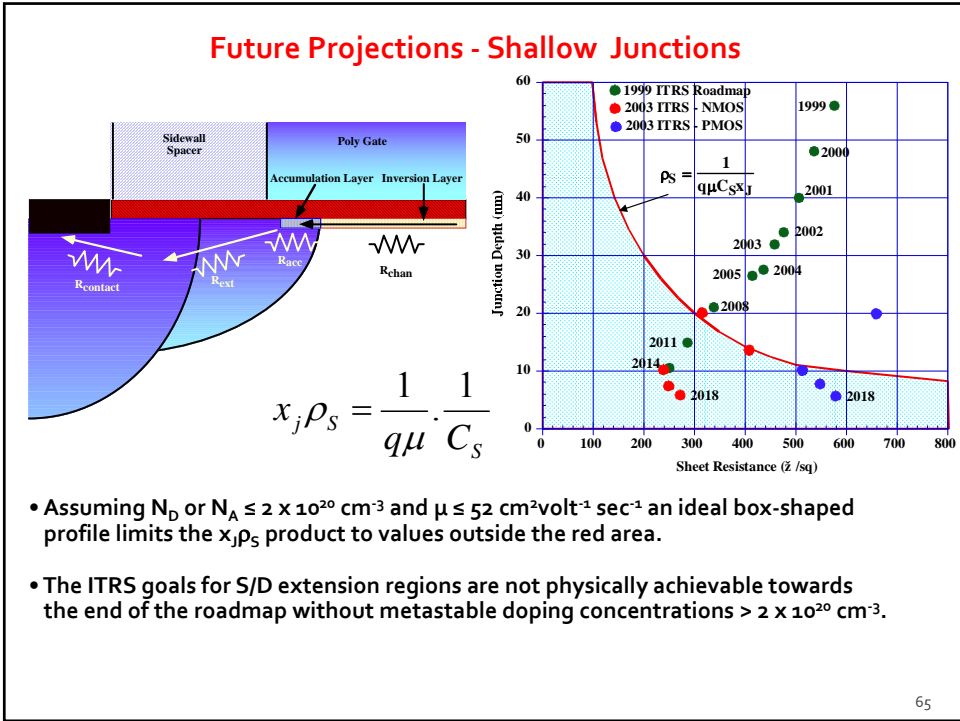












Summary of Key Ideas

- Selective doping is a key process in fabricating semiconductor devices.
- Doping atoms generally must sit on substitutional sites to be electrically active.
- Both doping concentration and profile shape are critical in device electrical characteristics.
- Ion implantation is the dominant process used to introduce dopant atoms. This creates damage and thermal annealing is required to repair this damage.
- During this anneal dopants diffuse much faster than normal.
- Atomistic diffusion processes occur by pairing between dopant atoms and point defects.
- In general diffusivities are proportional to the local point defect concentration.
- Point defect concentrations depend exponentially on temperature, and on Fermi level, ion implant damage, and surface processes like oxidation.
- As a result dopant diffusivities depend on time and spatial position during a high temperature step.
- Powerful simulation tools exist today which model these processes and which \therefore can predict complex doping profiles.

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Assignment #1 (due 16th April)

- Campbell: Problems
(Use text data rather than lecture slides)

2.7	3.5
2.8	3.7
2.11	3.8
2.13	3.14

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Practical Diffusions

Low concentrations:

- surface concentration in equilibrium with ambient gas

High concentrations (e.g. emitter diffusion) :

- surface concentration = solid solubility in wafer
- supplied from surface film

Limited source diffusions(e.g. base diffusion)

- Finite thickness film on wafer surface
- all consumed, typically less than monolayer
- ion implantation
- Infinite source diffusion for short time (pre-deposition) to establish limited source quantity Q
- low surface concentration and deep diffusion

D=f(N) - not constant

Generally needs computer simulation

Constant/infinite source diffusion

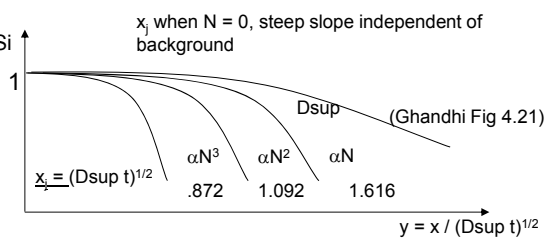
--> profile more abrupt than for constant D

$$D_0 = D_0 = D_{swp}$$

$$D_1 = K_1 D_0 N = D_{swp} (N/N_{swp}) \text{ as for As in Si}$$

$$D_2 = K_2 D_0 N^2 = D_{swp} (N/N_{swp})^2$$

$$D_3 = K_3 D_0 N^3 = D_{swp} (N/N_{swp})^3$$



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

Have recurring normalization factor $x/t^{1/2}$ above

$$\text{Define } z = x/2t^{1/2}$$

$$\frac{\partial z}{\partial x} = (1+2t^{1/2})^{-1} dx \quad \therefore \frac{\partial N}{\partial x} = (\frac{\partial N}{\partial z}) / 2t^{1/2}$$

$$\frac{\partial z}{\partial t} = (x/2)(-t^{-3/2}/2) dt \quad \therefore \frac{\partial N}{\partial t} = -x(\frac{\partial N}{\partial z}) / 4t^{3/2}$$

$$\text{Substitute gives } -2z (dN/dz) = d/dz (D (dN/dz))$$

i.e. ordinary differential equation

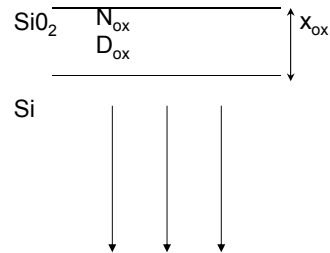
Solve for different situations and boundary conditions

e.g. for constant source diffusion (D varying)

At $x=0$, $N=N_{swp}$ and $z=0$ for all t

At $t=0$, $z=\infty$ for all x , and initial $N=N_1$

Other Useful Cases : Diffusion from doped oxide (spin-on glass)



M = impurity segregation coefficient at interface

For short times $x_{ox} \rightarrow 4\sqrt{(Dt)}$,

For approx constant source

i.e. oxide still supplies impurities as $t \rightarrow \infty$

$$N(x,t) \approx N_{ox} [D_{ox}/D (1+k)]^{1/2} \operatorname{erfc} x / (4Dt)^{1/2}$$

$$\text{where } k = (D_{ox}/D)^{1/2}$$

General Diffusion Solution #1

• Diffusion into semi-infinite substrate with initial distribution $N(x,0)=f(x)$

• Assume D constant $\rightarrow \partial N/\partial t = D \partial^2 N/\partial x^2$

• Separation of variables: $N(x,t) = X(x)T(t)$

$$\rightarrow \partial(XT)/\partial t = D \partial^2(XT)/\partial x^2$$

$$\rightarrow X(\partial T/\partial t) = DT(\partial^2 X/\partial x^2)$$

$$\rightarrow (1/DT) \partial T/\partial t = (1/X) (\partial^2 X/\partial x^2) = -\lambda^2$$

$$\partial T/T = -\lambda^2 D \partial t \quad \& \quad \partial^2 X/\partial x^2 = -\lambda^2 X$$

$$T(t) = \gamma \exp -\lambda^2 Dt \quad \& \quad X(x) = \alpha \cos \lambda x + \beta \sin \lambda x$$

$$\therefore N(x,t) = \exp -\lambda^2 Dt (A \cos \lambda x + B \sin \lambda x)$$

• General solution = \sum_{λ} all possible solutions

$$\therefore N(x,t) = \int_{-\infty}^{\infty} \exp -\lambda^2 Dt (A \cos \lambda x + B \sin \lambda x)$$

• and at $t=0$,

$$N(x,0) = \int_{-\infty}^{\infty} (A \cos \lambda x + B \sin \lambda x) d\lambda = f(x)$$

• Compare Fourier Integral Theorem:

$$f(x) = (1/2\pi) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\xi) \cdot \cos \lambda(\xi-x) d\xi d\lambda$$

$$= (1/2\pi) \int_{-\infty}^{\infty} \{ \int_{-\infty}^{\infty} f(\xi) \cdot \cos \lambda \xi d\xi \} \cos \lambda x + \{ \int_{-\infty}^{\infty} f(\xi) \cdot \sin \lambda \xi d\xi \} \sin \lambda x \} d\lambda$$

$$\text{• By comparison: } A = (1/2\pi) \int_{-\infty}^{\infty} f(\xi) \cos \lambda \xi d\xi, \quad B = (1/2\pi) \int_{-\infty}^{\infty} f(\xi) \sin \lambda \xi d\xi$$

$$\therefore N(x,t) = (1/2\pi) \int_{-\infty}^{\infty} f(\xi) \left[\int_{-\infty}^{\infty} \exp(-\lambda^2 4Dt) \cos \lambda(\xi-x) d\lambda \right] d\xi$$

$$= (2\sqrt{\pi Dt})^{-1} \int_{-\infty}^{\infty} f(\xi) \exp(-(\xi-x)^2/4Dt) d\xi$$

$$= (2\sqrt{\pi Dt})^{-1} \int_{-\infty}^{\infty} N(\xi,0) \exp(-(\xi-x)^2/4Dt) d\xi$$

Time Dependent Diffusion

If $D=D(t)$, e.g. for $T=T(t)$

e.g. furnace insertion/withdrawal

write $\partial \tau = D(t) \partial t$

i.e. $\tau = \int_{t_0}^t D(t) dt = (Dt)_{\text{eff}}$

and $D^{-1} (\partial N / \partial t) = \partial^2 N / \partial x^2$

--> $\partial N / \partial \tau = \partial^2 N / \partial x^2$

$$(Dt)_{\text{eff}} = \int_{t_0}^t D(t) dt$$

$$= \int_{t_0}^t D_0 \exp -E_0/kT(t) dt$$

$$= \int_{t_0}^t D_0 \exp -(E_0/kT_0)(1+Ct/T_0) dt$$

$$= \int_{t_0}^t D(T_0) \exp -(CE_0/kT_0^2)t \cdot dt$$

$$= D(T_0) [(1-\exp-(CE_0/kT_0^2)t_0)] / (CE_0/kT_0^2)$$

$$\approx D(T_0) [kT_0^2 / CE_0] \text{ if } t_0 \rightarrow \infty$$

Assume linear $T(t)$ variation

- i.e. $T=T_0-Ct$ (ramp down)

$$T^{-1} = (T_0 - Ct)^{-1}$$

$$= T_0^{-1} (1 - Ct/T_0)^{-1}$$

$$\approx T_0^{-1} (1 + Ct/T_0) \text{ for } T_0 \gg Ct$$

Additional effective time kT_0^2 / CE_0 at temp T_0

due to a slow ramp-down

Note: ramp-up --> symmetrical effective time

e.g. for $T_0=900^\circ\text{C}$, $E_0=4\text{eV}$, $C=900^\circ\text{C}/20\text{min}$

$$\Delta t = 1.38 \times 10^{-23} (1173)^2 20 / 900.4 (1.6 \times 10^{-25}) \approx 45\text{s}$$

Account for ramp-down: extra 45sec at 900°C

Dissociation

(Mixed diffusion revisited)

• $S \rightleftharpoons I + V$
Substitutional Interstitial Vacancy

Interstitial $D_i' \gg D_s$ substitutional, \therefore assume substitutional impurities immobile

Region of high concentration

Interstitials move out faster,
 \therefore Equation driven $L \rightarrow R$
 \therefore many substitutional impurities
convert to interstitial & also move out
 \therefore High apparent D

Region of low concentration:

More Interstitials moving in than substitutional
 \therefore Equation driven $R \rightarrow L$
 \therefore Interstitials convert to substitutionals
& move more slowly
 \therefore Low apparent D

Two extreme cases for low concn. region ($S \leftarrow I + V$):

• Semiconductor highly dislocated

lots of vacancies, reaches equilibrium quickly

More Interstitials moving in than substitutionals

$$v_{\text{eff}} \sim v_i N_i / (N_i + N_s) \rightarrow D_{\text{eff}} \sim D_i' N_i / (N_i + N_s)$$

• Low dislocation density

Equilibrium slow & equation $R \rightarrow L$

(limited by low vacancy conc'n)

$\therefore N_i$ is equilibrium value

$$v_{\text{eff}} \sim v_v n_v / (n_v + n_s) \rightarrow D_{\text{eff}} \sim D_v n_v / n_s$$

where D_v = self-diffusivity of Si atoms

Substitutional Impurity Diffusion

$$\delta(N_s + N_i)/\delta t = \partial(D_s' \cdot \partial N_s / \partial x + D_i' \cdot \partial N_i / \partial x) / \partial x$$

for $N_s \gg N_i \rightarrow$

$$\partial N_s / \partial t \approx \partial[(D_s' + D_i' \cdot \partial N_i / \partial N_s)(\partial N_s / \partial x)] / \partial x$$

i.e. for substitutional impurity diffusion

$$\text{effective } D \approx D_s' + D_i' \left(\frac{\partial N_i}{\partial N_s} \right)$$

$$\approx (D_i') \left(\frac{\partial N_i}{\partial N_s} \right) \text{ for } D_i' \gg D_s'$$

and $\partial N_i / \partial N_s$ depends on the dissociation mechanism

As in Si

$$D_{\text{eff}} = h [D_i^0 + D_i^+ (p/n_i) + D^- (n/n_i) + D^2 (n/n_i)^2 \dots]$$

For As, there are As(I-V⁰) & As(I-V⁻) levels

$$\therefore D = h[D_i^0 + D_i^- (n/n_{ie})]$$

n_{ie} = intrinsic electron concentration at high N_D

(solid solubility limited, i.e. $N_D \gg n_{ie}$)

$$\& h = 2, \therefore D \approx 2 D_i^- (N_D/n_{ie})$$

This is 1st-order conc'n dependent diffusion

[see back; compare $D = K_1 D_0 N = D_{\text{surf}} (N/N_{\text{surf}})$]

EITHER use previous result $x_j = 2D_i^- (N_{\text{surf}}/n_{ie})$

$$x_j = 1.616 (D_{\text{surf}} t)^{1/2}$$

$$x_j = 1.616 (2D_i^- (N_{\text{surf}}/n_{ie}) t)^{1/2}$$

$$x_j = 2.29 (N_{\text{surf}}/n_{ie})^{1/2} (D_i^- t)^{1/2}$$

$$\text{where } D_i^{\pm} = 22.9 \exp(-4.1 \text{ eV}/kT)$$

OR solve $D = 2D_i^- (N/n_{ie})$ in closed form \rightarrow

$$N = N_{\text{surf}} (1 - 0.87y - 0.45y^2) \text{ where } y = x(4D_{\text{surf}} t)^{1/2}$$

B in Si

Low surface conc'n --> use constant D

High conc'n --> B(I-V⁰), B(I-V⁺) levels

$$\therefore D = h[D_i^0 + D_i^+ (p/n_i)]$$

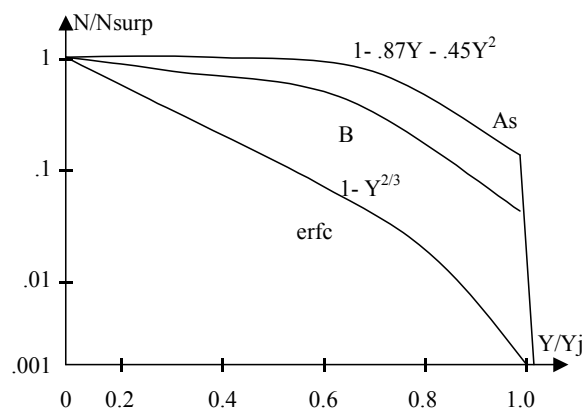
n_i not significantly affected by N_A

usually $h \sim 1$, $D = 3.17 \exp(-3.59\text{eV}/kT)$

EMPIRICALLY: $x_j \cong 2.45(N_{\text{surf}}/n_i)^{1/2} (Dt)^{1/2}$

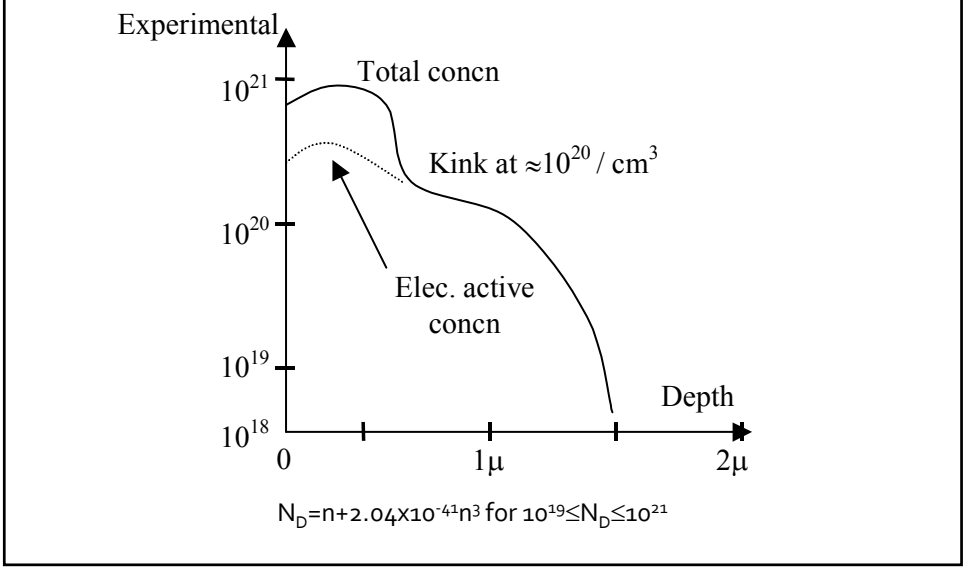
OR: $N \cong N_{\text{surf}}(1 - y^{2/3})$, where $y = (x^2/6D_{\text{surf}}t)^{3/2}$

Boron & Arsenic in Silicon



B, As doping profiles with inclusion of defect charge effects
(Note similarity to diffusion with $D \propto N$)

P in Si



P in Si (idealized model)

