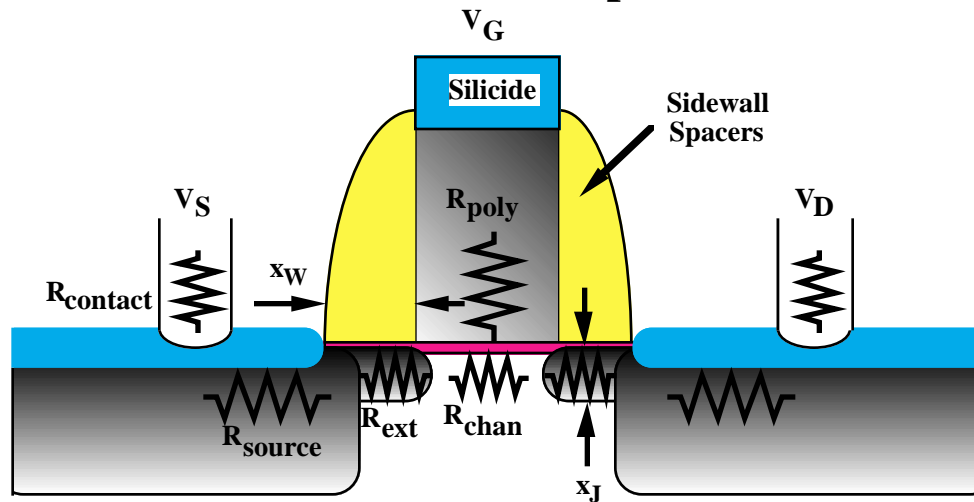# EE 212 FALL 1999-00

DIFFUSION - Chapter 7

Basic Concepts

- **Placement of doped regions (main source/drain, S/D extensions, threshold adjust) determine many short-channel characteristics of a MOS device.**
- **Resistance impacts drive current.**
- **As device shrinks by a factor K, junction depths should also scale by K to maintain same $\mathcal{E}$-field patterns (assuming the voltage supply also scales down by the same factor).**
- **Gate doping affects poly-depletion and limits how the gate voltage controls the channel potential.**

a) $R = \rho$

b) $\rho_S = \rho/x_j$
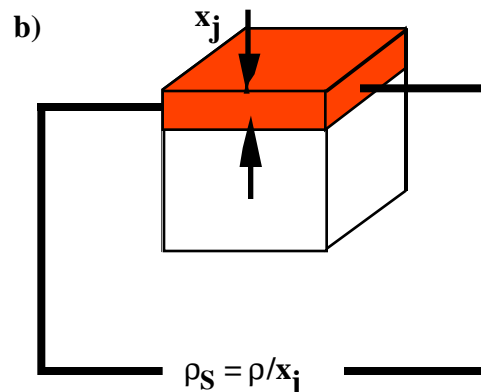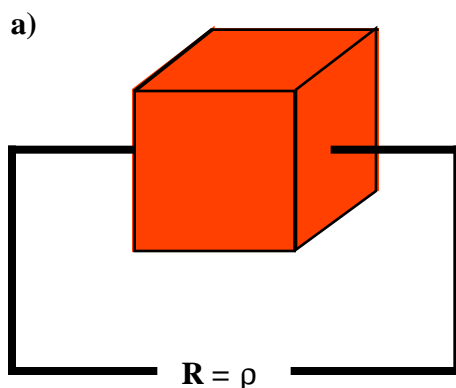
- **The resistivity of a cube is given by**

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

- **The sheet resistance of a shallow junction is**

$$\mathbf{R} = \frac{\rho}{\mathbf{x_j}} \ \Omega/\mathbf{Square} \equiv \rho_S \qquad (2)$$

- **For a non-uniformly doped layer,**

$$\rho_s = \frac{\rho}{\mathbf{x_j}} = \frac{1}{\mathbf{q} \int\limits_0^{\mathbf{x_j}} \left[\mathbf{n(x)} - \mathbf{N_B}\right] \mu[\mathbf{n(x)}] \, \mathbf{dx}} \qquad (3)$$

- **This equation has been numerically integrated by Irwin for different analytical profiles (later).**

- **Sheet resistance can be experimentally measured by a four point probe technique.**

Year of 1st DRAM Shipment	1997	1999	2003	2006	2009	2012
Min Feature Size	0.25µ	0.18µ	0.13µ	0.10µ	0.07µ	0.05µ
DRAM Bits/Chip	256M	1G	4G	16G	64G	256G
Minimum Supply Voltage (volts)	1.8-2.5	1.5-1.8	1.2-1.5	0.9-1.2	0.6-0.9	0.5-0.6
Gate Oxide T_{ox} Equivalent (nm)	4-5	3-4	2-3	1.5-2	<1.5	<1.0
Sidewall Spacer Thickness x_W (nm)	100-200	72-144	52-104	20-40	7.5-15	5-10
Contact x_j (nm)	100-200	70-140	50-100	40-80	15-30	10-20
x_i at Channel (nm)	50-100	36-72	26-52	20-40	15-30	10-20
Drain Ext Conc (cm^{-3})	1x10^{18}	1x10^{19}	1x10^{19}	1x10^{20}	1x10^{20}	1x10^{20}

• **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 junction depth and surface concentration.**

"Predep" controlled dose

Drive-in constant dose

Silicon
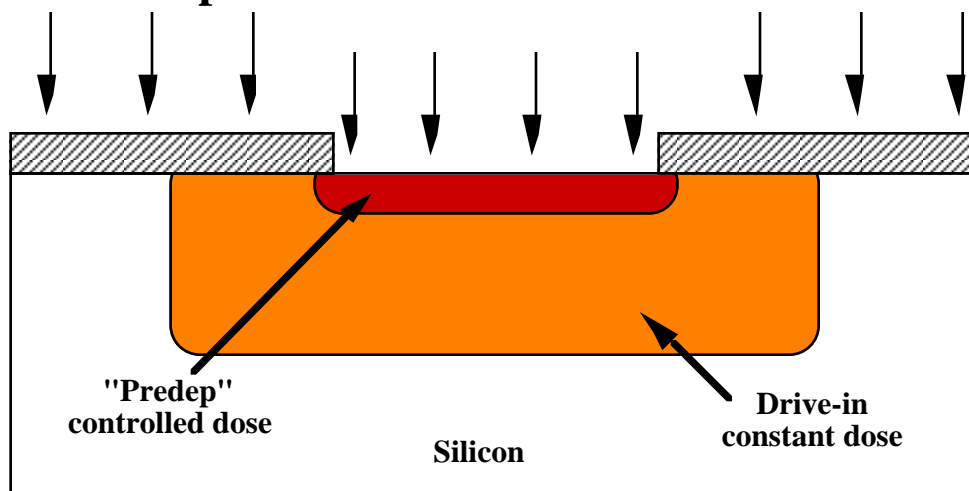
	Ion Implantation and Annealing	Solid/Gas Phase Diffusion
Advantages	Room temperature mask	No damage created by doping
	Precise dose control	Batch fabrication
	10^{11} - 10^{16} atoms cm^{-2} doses	
	Accurate depth control	
Problems	Implant damage enhances diffusion	Usually limited to solid solubility
	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 predeps very difficult

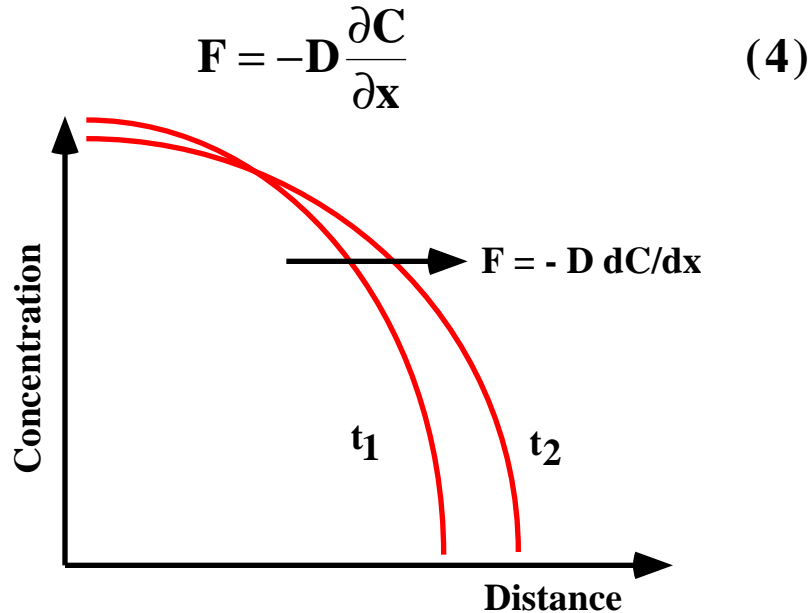• **Dopants are soluble in bulk silicon up to a maximum value before they precipitate into another phase.**
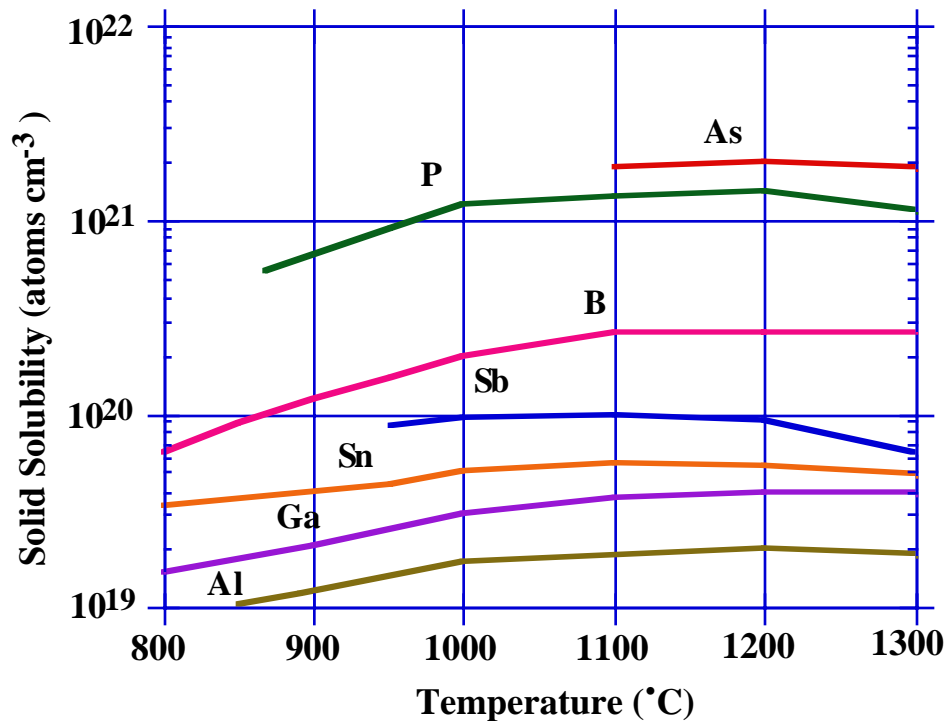
• **Dopants may have an "electrical" solubility that is different than the solid solubility defined above.**
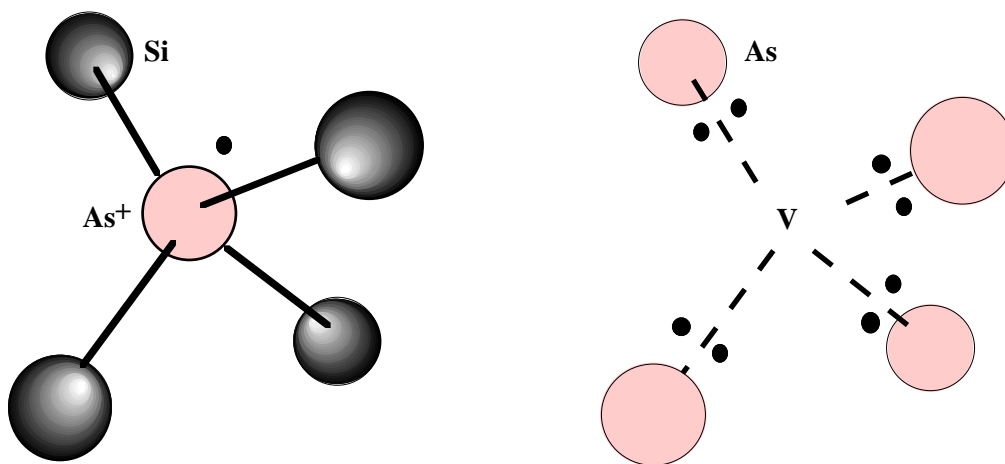

• **As$_4$V is one possible electrically inactive form.**

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

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

(Figure: plot of Concentration vs. Distance showing two red curves labeled t_1 and t_2, with an arrow labeled $F = - D \, dC/dx$)

- **This is similar to other laws where cause is proportional to effect (Fourier's law of heat flow, Ohm's law for current flow).**

- **Proportionality constant is the diffusivity D in cm^2 sec^{-1}. D is related to atomic hops over an energy barrier (formation and migration of mobile species) and is exponentially activated. D is isotropic in the silicon lattice.**

- **Negative sign indicates that the flow is down the concentration gradient.**

- **Fick's second law describes how the change in concentration in a volume element is determined by the change in fluxes in and out of the volume.**
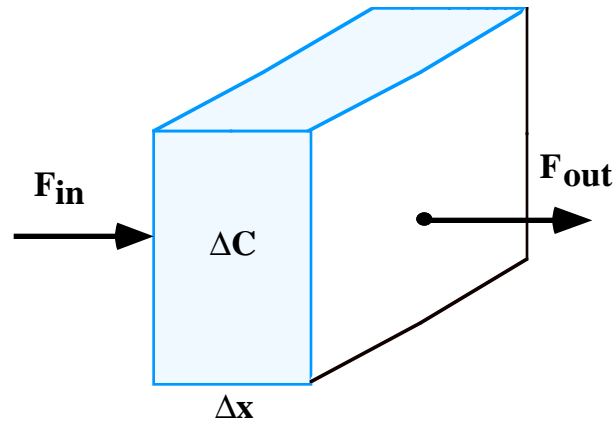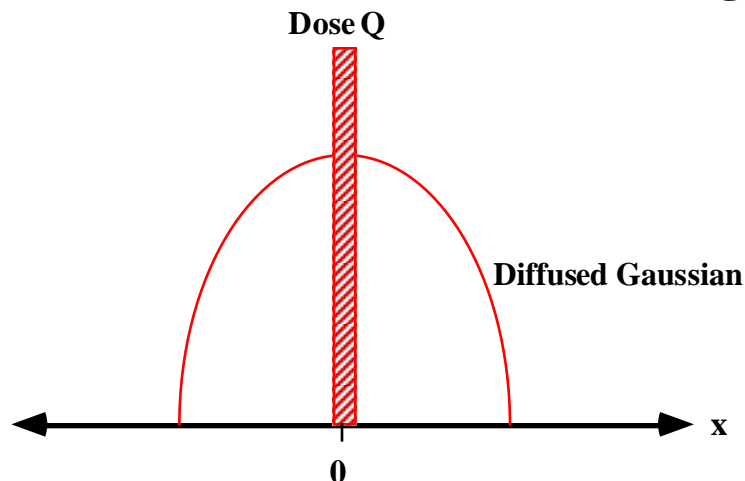
• **Mathematically**

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

• **If D is a constant this gives**

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (6)$$

Solutions Of Fick's Laws

**1. Limited Source: Consider a fixed dose Q,
   introduced as a delta function at the origin.**
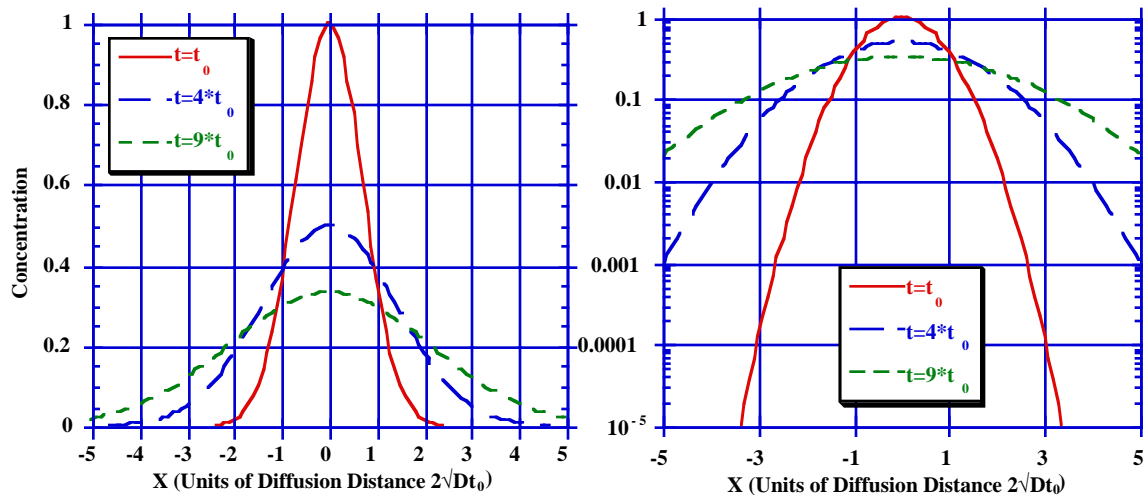
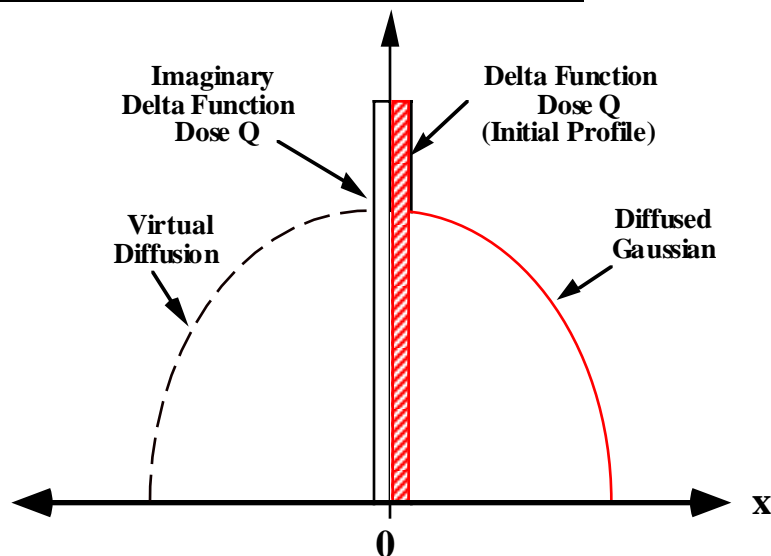- **The solution that satisfies Fick's second law is**

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

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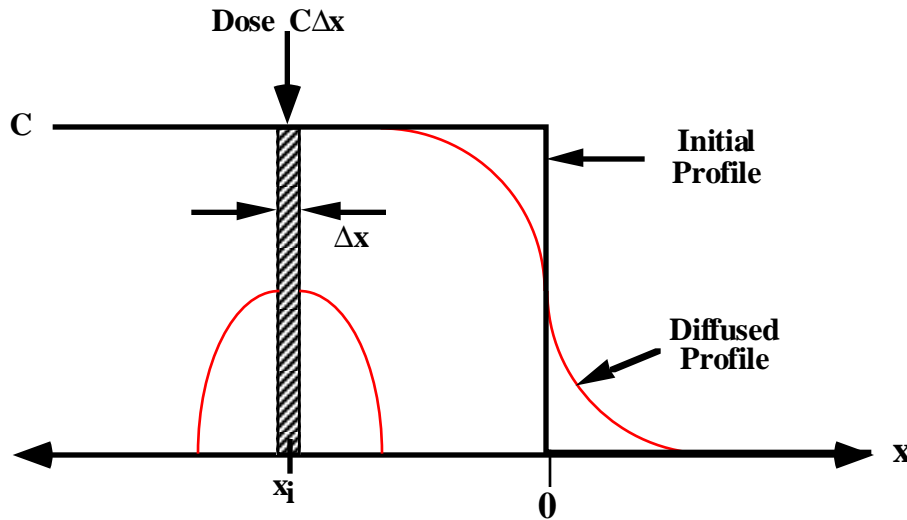3. **Diffusion distance from origin increases as** $2\sqrt{Dt}$

2. Constant Source Near A Surface:

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

3. Infinite Source: Consider an infinite source of dopant made up of small slices each diffusing as a Gaussian.

$$C(x,t) = \frac{C}{2\sqrt{\pi Dt}} \sum_{i=1}^{n} \Delta x_i \exp-\frac{(x-x_i)^2}{4Dt} \quad (9)$$

• **The solution which satisfies Fick's second law is**

$$C(x,t) = \frac{C'}{2}\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] = C_S\left[erfc\left(\frac{x}{2\sqrt{Dt}}\right)\right] \quad (10)$$

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.**
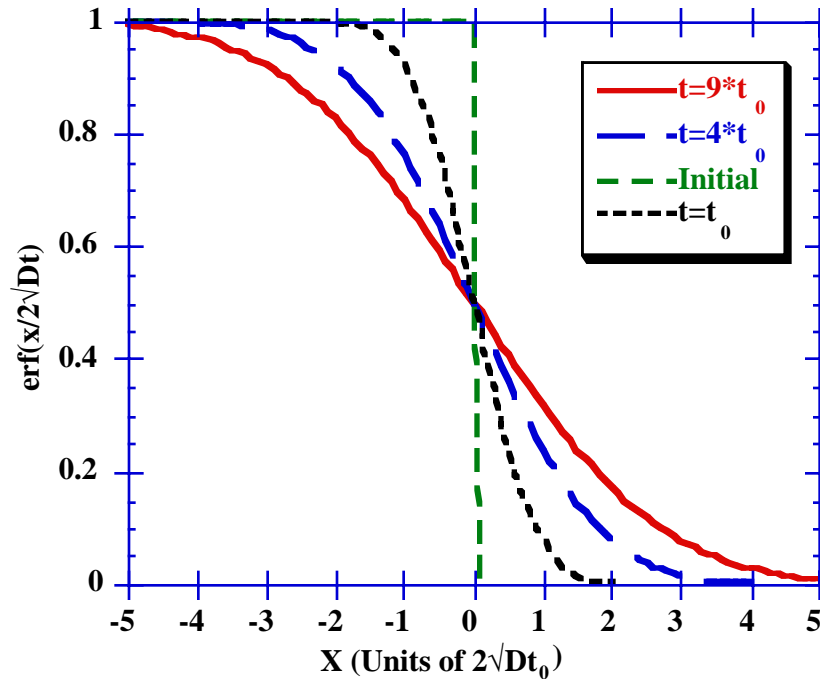
- **See Appendix in text for properties of erfc.**

4. Constant Surface Concentration: (just the right hand side of the above figure).

$$C(x,t) = C_S\left[\text{erfc}\,\frac{x}{2\sqrt{Dt}}\right] \qquad (11)$$

- **Note that the dose is given by**

$$Q = \int_0^\infty C_S\left[1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] = \frac{2C_S}{\sqrt{\pi}}\sqrt{Dt} \qquad (12)$$
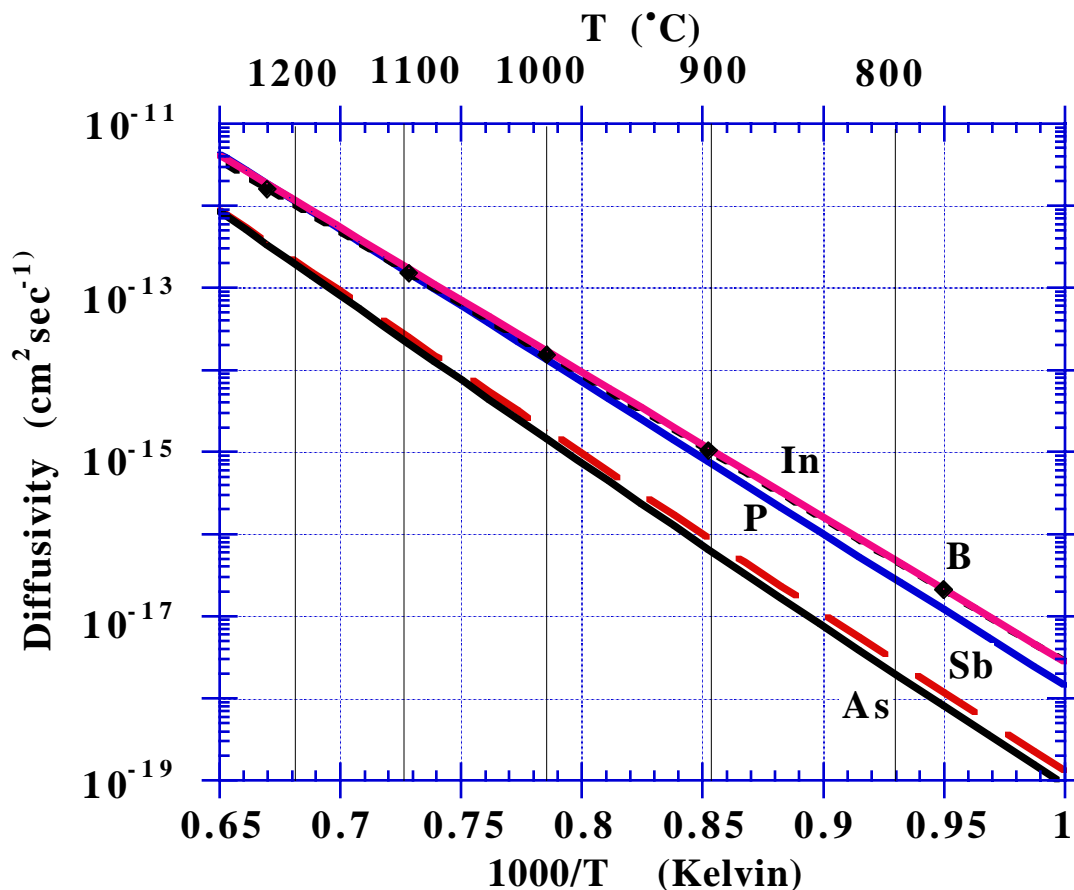
Intrinsic Dopant Diffusion Coefficients

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

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

	Si	B	In	As	Sb	P	Units
D^0	560	1.0	1.2	9.17	4.58	4.70	cm^2 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 dopant for a particular application.**

Effect Of Successive Diffusions

- **If a dopant is diffused at temperature T1 for time t1 and then is diffused at temperature T2 for time t2, the total effective Dt is given by the sum of all the individual Dt products.**

$$\mathbf{Dt_{eff} = \sum Dt = D_1 t_1 + D_2 t_2 + ...} \qquad (14)$$

- **Some of the Dt steps may be negligible in a process.**

- **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 junction for the emitter-base occurs when**

$$\mathbf{C_S erfc\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{Q}{\sqrt{\pi Dt}} exp\left(-\frac{x^2}{4Dt}\right)} \quad (15)$$
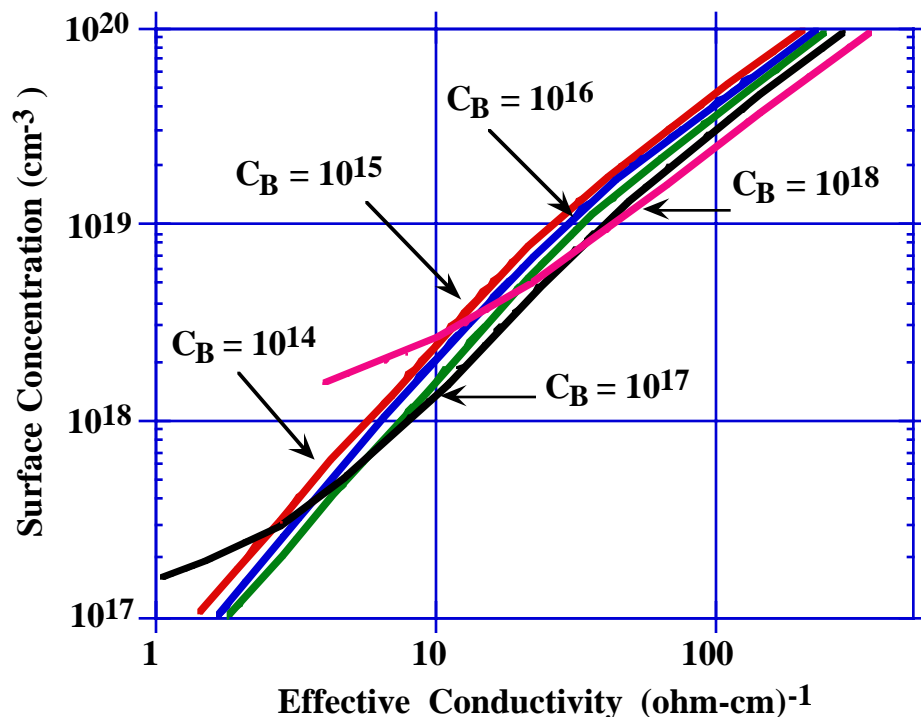
(Emitter Dt)   **(Base+Emitter Dt)**

and the collector-base junction occurs when

$$\frac{Q}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) = C_B$$

Design Of Diffused Layers

- **Eqn. (3) has been numerically integrated for specific cases (erfc and Gaussian).**

- **Example of Irvin's curves below, 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 - Figs. 2.10 - 2.12), such that**

$$\rho_S = 900 \ \Omega/\text{square}$$

$$x_j = 3 \ \mu m$$

$$N_{BC} = 1x10^{15} \ cm^{-3} \ (\text{substrate concentration})$$

- **The average conductivity of the layer is**

$$\bar{\sigma} = \frac{1}{\rho_S x_j} = \frac{1}{(900\Omega/sq)(3\times10^{-4}cm)} = 3.7 \ (\Omega\cdot cm)^{-1}$$

- **From Irvin's curve we obtain**

$$C_S \approx 4\times10^{17}/cm^3$$

- **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

$$Dt = \frac{X_j^2}{4\ln\frac{C_s}{C_{bc}}} = \frac{\left(3x10^{-4}\right)^2}{4\ln\left(\frac{4x10^{17}}{10^{15}}\right)} = 3.7x10^{-9} cm^2$$

- **If the drive-in is done at 1100 °C, then the boron diffusivity is $D = 1.5\times10^{-13} \ cm^2 \ sec^{-1}$.**

- **The drive-in time is therefore**

$$t_{drive-in} = \frac{3.7 \times 10^{-9} \, cm^2}{1.5 \times 10^{-13} \, cm^2/sec} = 6.8 \, hours$$

- **Given both the surface concentration and the Dt product, the initial dose can be calculated for this Gaussian profile.**

$$Q = C_S \sqrt{\pi Dt} = \left(4 \times 10^{17}\right)\left(\sqrt{\pi}\right)\left(\sqrt{3.7 \times 10^{-9}}\right) = 4.3 \times 10^{13} \, cm^{-2}$$

- **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 predeposition step at 950˚C were used**

  B solid solubility at 950 ˚C is $2.5 \times 10^{20} \, cm^{-3}$
  B diffusivity is $4.2 \times 10^{-15} \, cm^2 \, sec^{-1}$

- **The dose for an erfc profile is**

$$Q = \frac{2C_s}{\sqrt{\pi}} \sqrt{Dt}$$

so that the time required for the predeposition is

$$t_{pre-dep} = \left(\frac{4.3 \times 10^{13}}{2.5 \times 10^{20}}\right)^2 \left(\frac{\sqrt{\pi}}{2}\right)^2 \frac{1}{4.2 \times 10^{-15}} = 5.5 \, sec$$
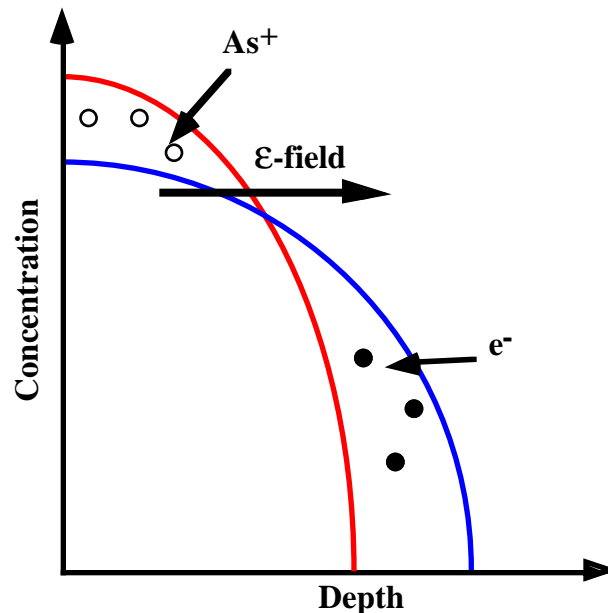
Check:

$$\textbf{Dt}_{\textbf{predep}}\left(2.3 \times 10^{-14}\right) \ll \textbf{Dt}_{\textbf{drive-in}}\left(1.5 \times 10^{-13}\right)$$

Modifications Of Fick's Laws

A. Electric field effects

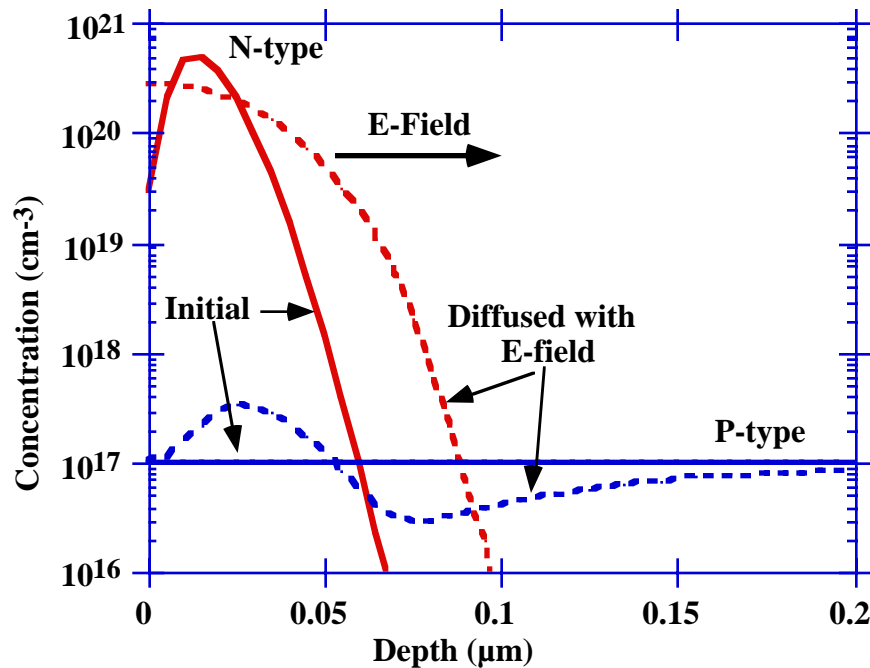- **When the doping is higher than n_i, $\mathcal{E}$-field effects become important.**

- **$\mathcal{E}$-field induced by higher mobility of electrons and holes compared with dopant ions.**
- **$\mathcal{E}$-field enhances the diffusion of dopants causing the field (see derivation in text).**
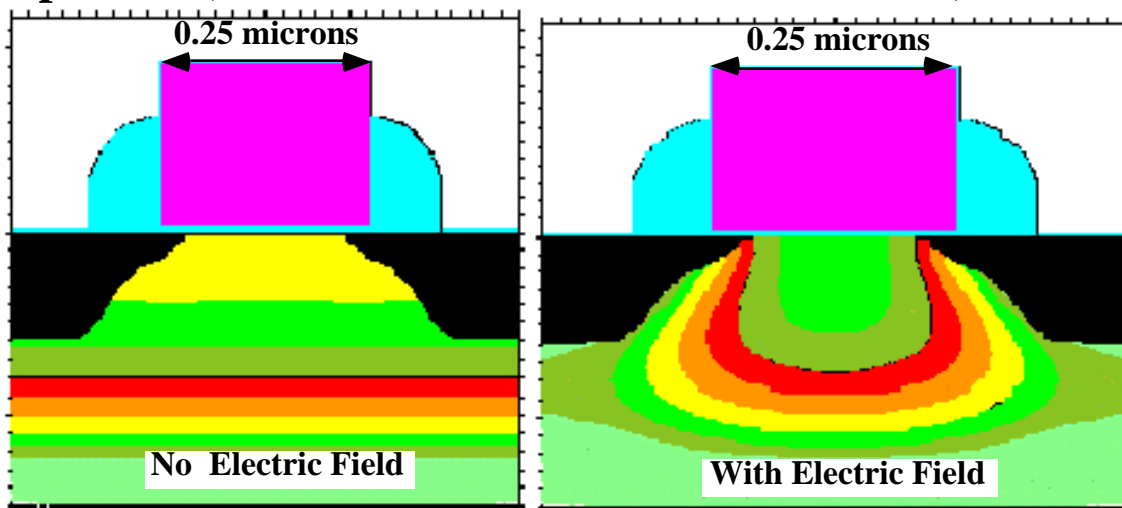
$$J = -hD_A \frac{\partial C}{\partial x} \qquad (16)$$

where

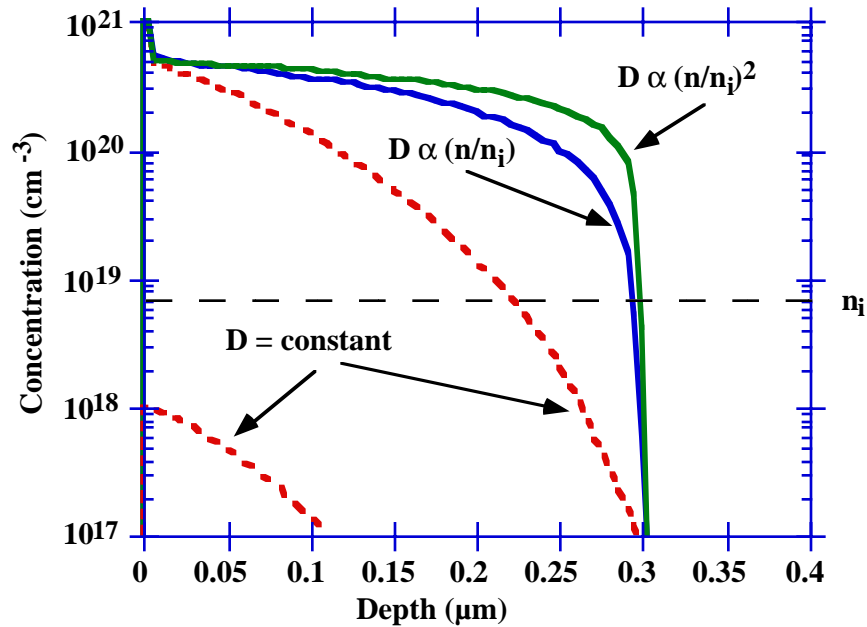$$h = 1 + \frac{C}{\sqrt{C^2 + 4n_i^2}} \qquad (17)$$

- **SUPREM simulation at 1000°C. Note the boron profile (h ≤ 2 for the As but dominates B).**

- **Field effects can dominate the doping distribution near the source/drain of a MOS device (SUPREM simulation).**

B. Concentration Dependent Diffusivity

- **At high doping concentrations, the diffusivity appears to increase. Fick's equation must then be solved numerically since D ≠ constant.**

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

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

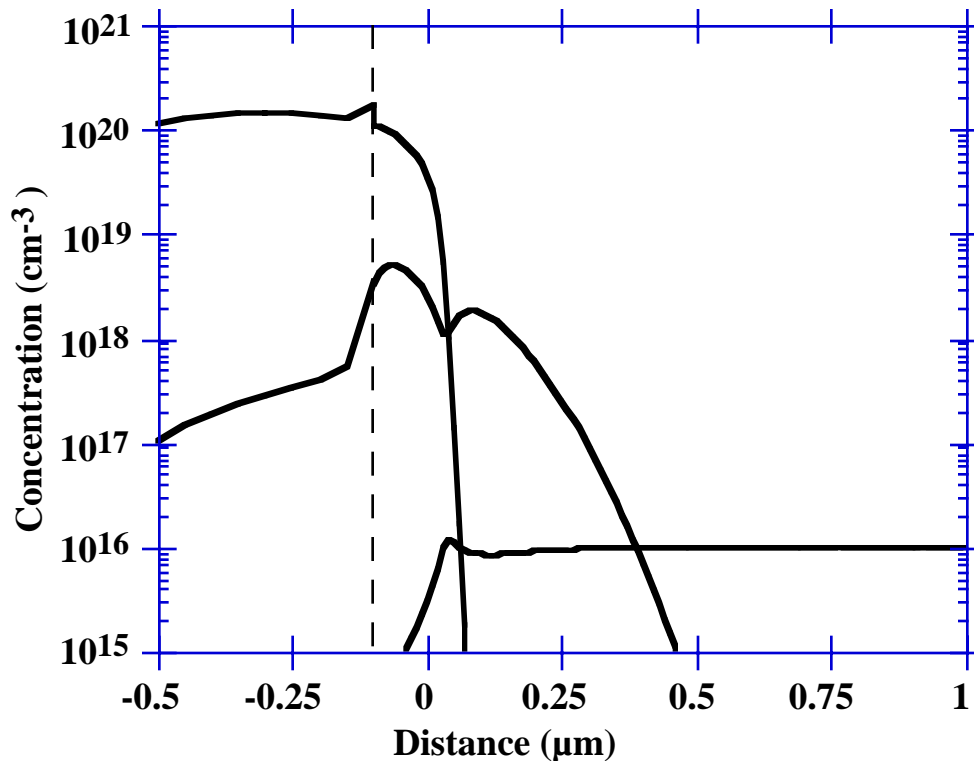- **Often, D is well described by**

$$D_A^{eff} = D^0 + D^-\left(\frac{n}{n_i}\right) + D^=\left(\frac{n}{n_i}\right)^2 \qquad (18)$$

$$D = D.0\exp\left(-\frac{D.E}{kT}\right) \qquad (19)$$

	Si	B	In	As	Sb	P
$D^0.0$	560	0.05	0.6	0.011	0.214	3.85
$D^0.E$	4.76	3.5	3.5	3.44	3.65	3.66
$D^+.0$		0.95	0.6			
$D^+.E$		3.5	3.5			
$D^-.0$				31.0	15.0	4.44
$D^-.E$				4.15	4.08	4.0
$D^=.0$						44.2
$D^=.E$						4.37

- **The n and n^2 (p and p^2 for P type dopants) terms are thought to be due to charged defect diffusion mechanisms.**
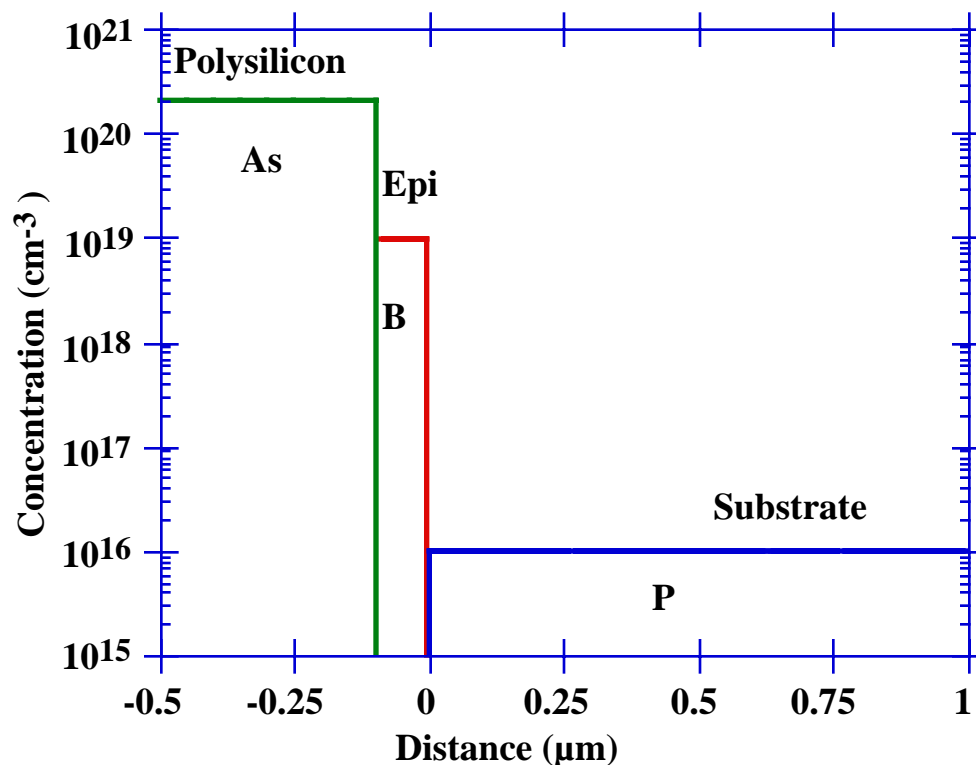
- **SUPREM simulation including ℰ-field and concentration dependent D effects.**
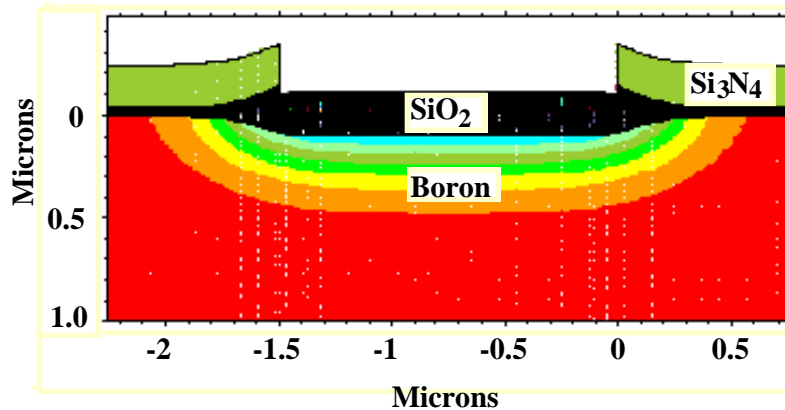
C. Segregation

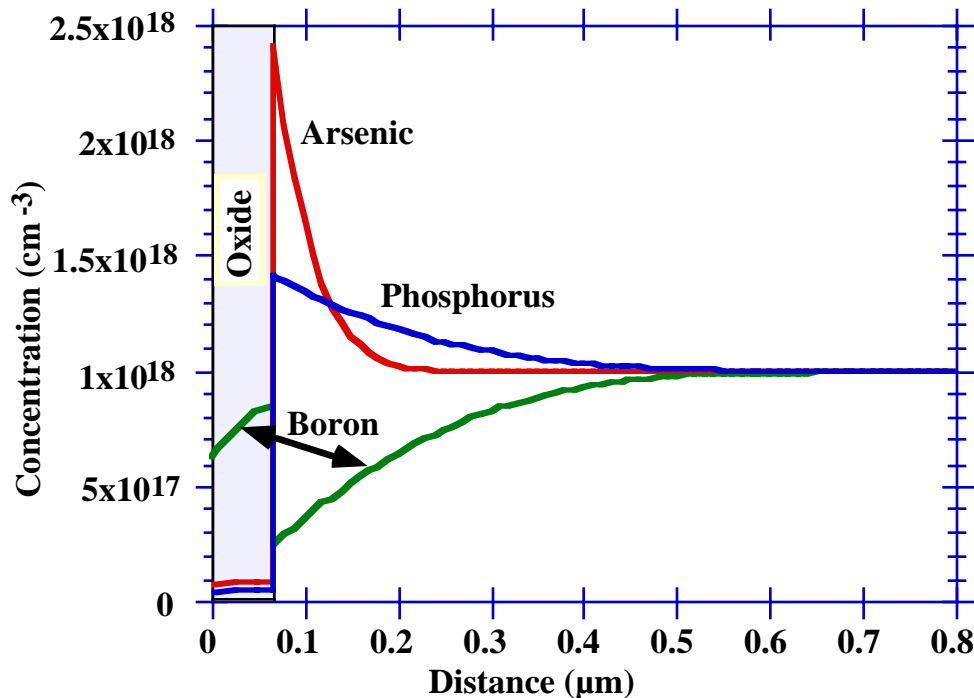- **Dopants segregate at interfaces. Recall from chapter 3,**

$$k_O = \frac{C_S}{C_L} \qquad (20)$$

- **This gives an interface flux of**

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

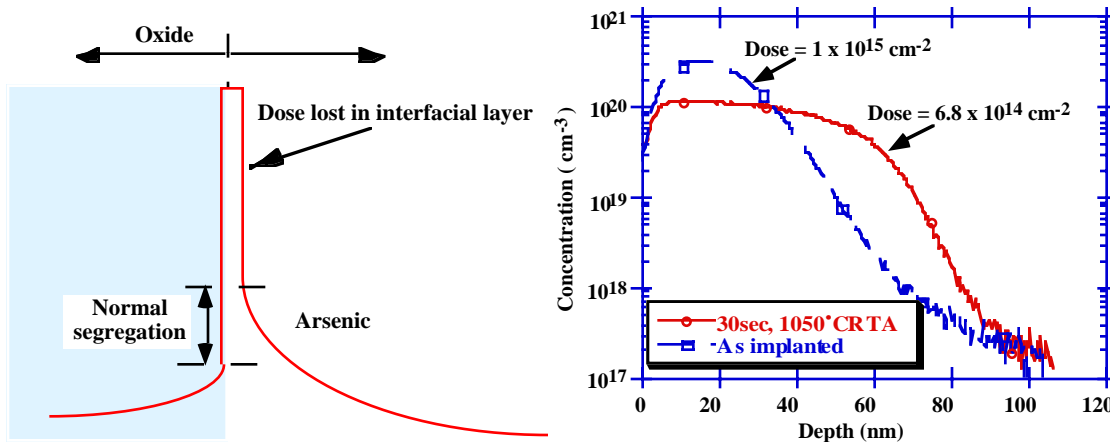- **Oxidation of a uniformly doped boron substrate depletes the boron into the growing SiO$_2$.**

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

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.**

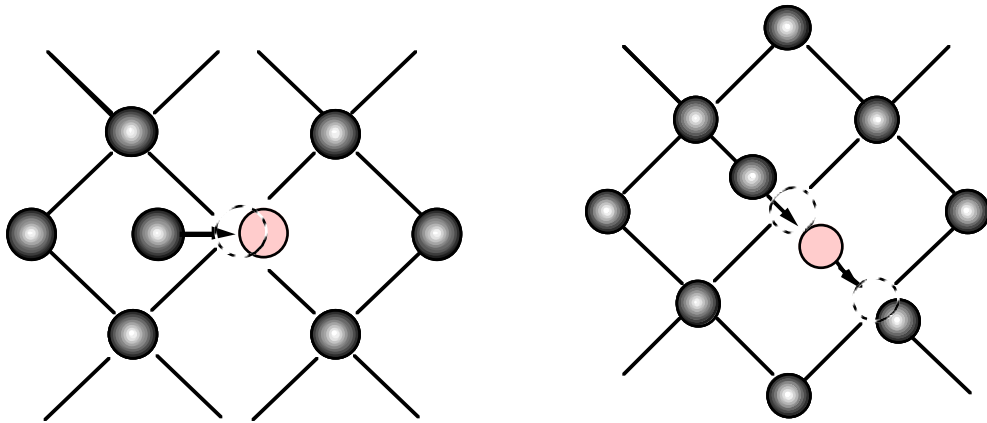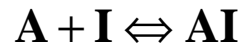- **In the experiment (right) 40% of the dose was lost in a 30 sec anneal.**

Atomic   Scale   Diffusion

- **Many effects (OED, TED etc) that are very important experimentally, cannot be explained by the macroscopic models discussed so far.**
- **Thus we need to look deeper at atomic scale effects.**

Vacancy Assisted Mechanism: $A + V \Leftrightarrow AV$
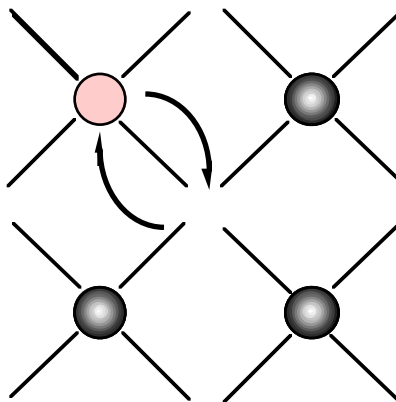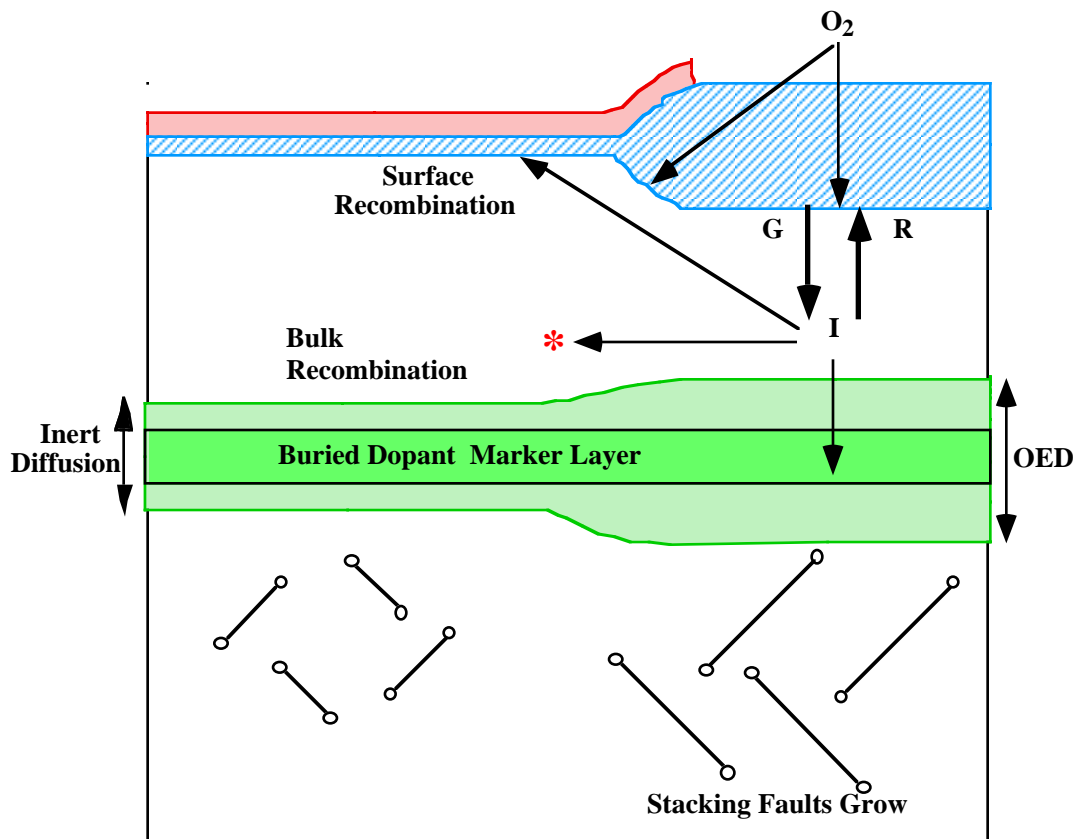
Kick-out and Interstitial(cy) Assisted Mechanisms

$$A + I \Leftrightarrow AI$$

## • These are identical from a math viewpoint.

A. Inferences About Mechanisms

- **Oxidation provides an I injection source.**
- **Nitridation provides a V injection source.**
- **Stacking faults serve as "detectors" as do dopant which diffuse.**

B. Modeling I And V Components Of Diffusion

- **Experiments like those above and the As/Sb experiment below have "proven" that both point defects are important in silicon.**
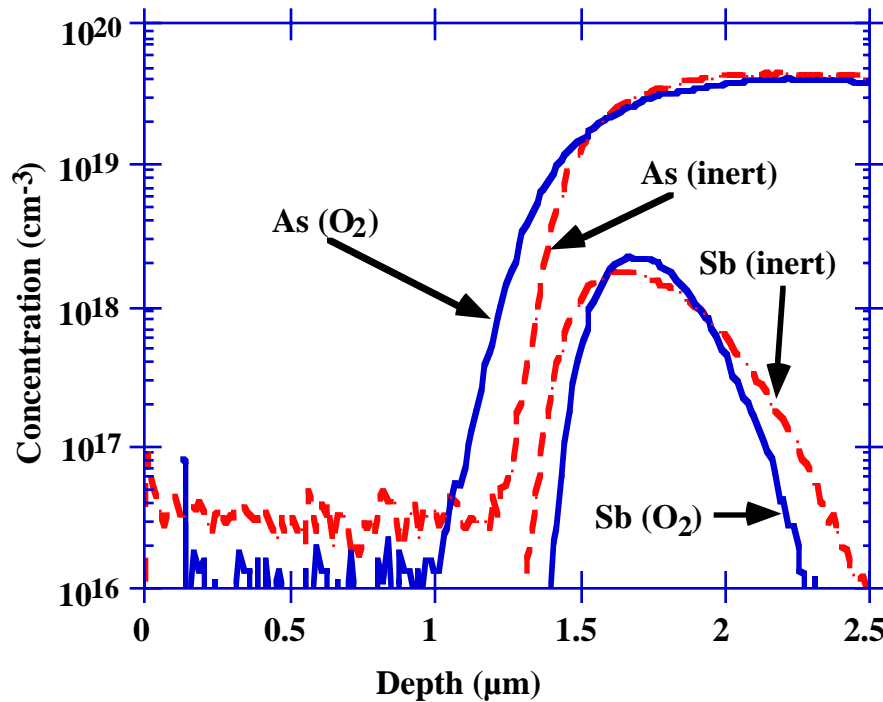
- **As a result, we can write**

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

- **Thus dopant diffusion can be enhanced or retarded by changes in the point defect concentrations.**

- **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.**

- **Measurements on the extent of enhanced or retarded diffusion of a dopant under oxidizing or nitriding conditions allow an estimate of the I or V component of diffusion to be made.**

|	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

C. Modeling Atomic Scale Reactions

- **Consider the simple chemical reaction**

$$A + I \longleftrightarrow AI \qquad\qquad (23)$$
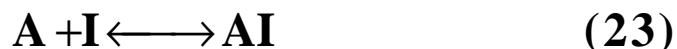
- **This contains a surprising amount of physics.**

- **For example OED is explained because oxidation injects I driving the equation to the right, creating more AI pairs and enhancing the dopant D.**

- **In the more complex example below, phosphorus diffuses with I, and releases them in the bulk. This enhances the tail region D.**
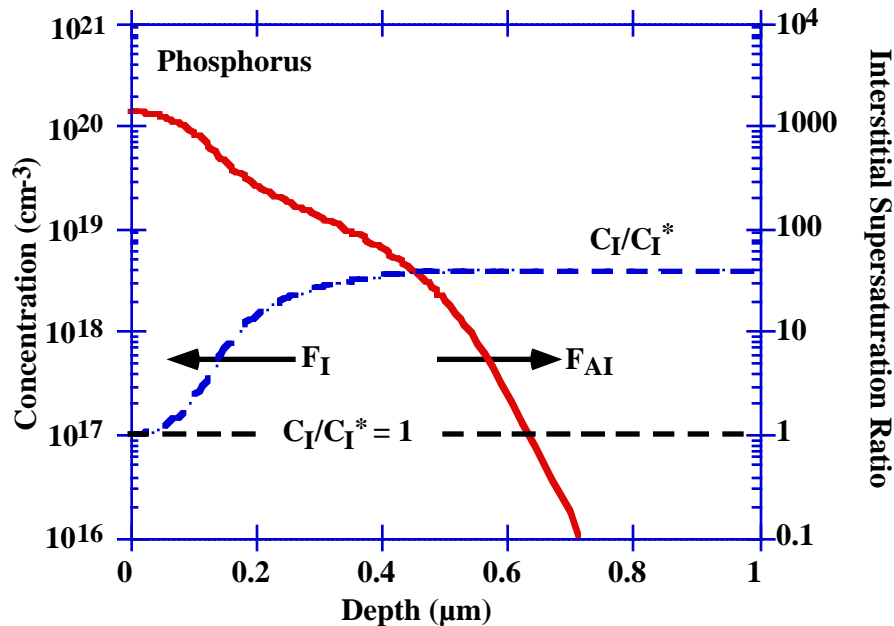
- **"Emitter push" is also explained by this mechanism.**
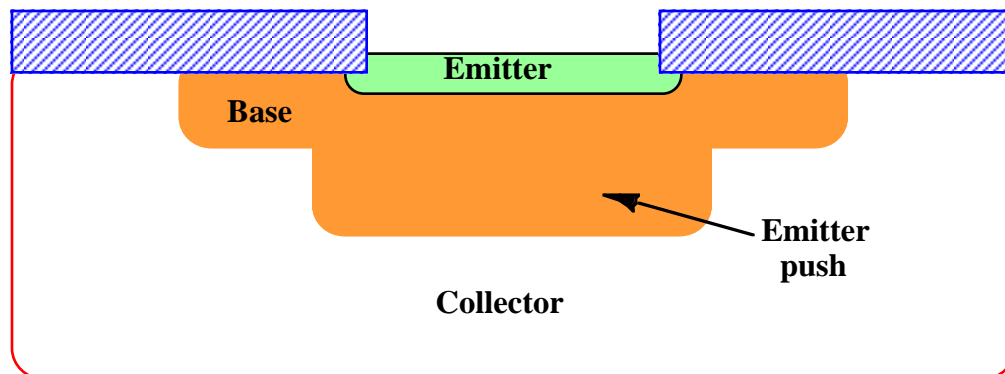
- **If we assume "chemical equilibrium" between dopants and defects in Eqn. (23), then from the law of mass action,**

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

- **Applying Fick's law to the _mobile species_**

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

- **Applying the chain rule from calculus**

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

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

- **The overall flux equation that is solved by simulators like SUPREM (see text for derivation)**

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

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

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

- **inert, low concentration diffusion, driven by the dopant gradient $\left(D_{BI}^{*}\right)$**

- **the interstitial supersaturation $(\dfrac{C_{I^o}}{C_{I^o}^{*}})$**

- **high concentration effects on the dopant diffusivity** $\left(1 + \beta \dfrac{p}{n_i}\right) / (1 + \beta)$

- **the electric field effect** $(\dfrac{\partial}{\partial x} \ln \dfrac{p}{n_i})$

- **Together, these provide a very powerful modeling capability in modern simulation tools.**
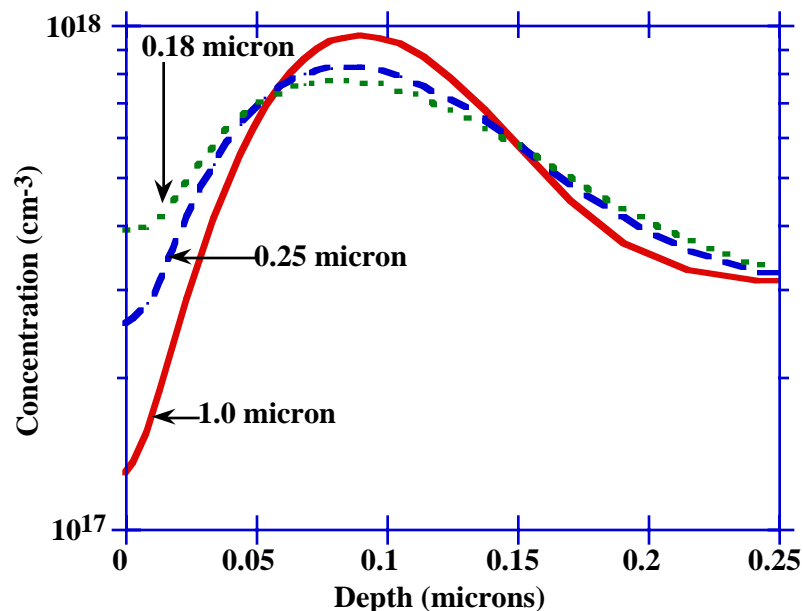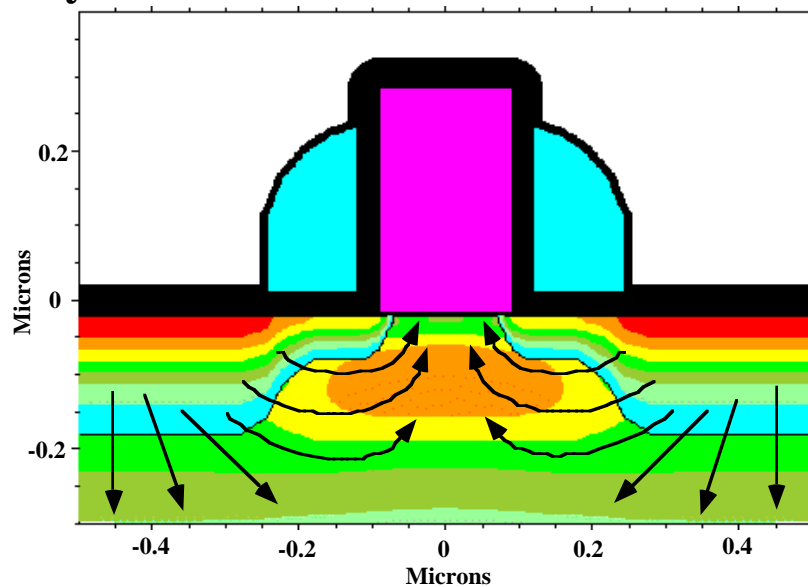
- **Example of a 2D SUPREM simulation of a small geometry MOS transistor.**

- **Ion implantation in the S/D regions generates excess I.**

- **These diffuse into the channel region pushing boron (channel dopant) up towards the surface.**

- **Effect is more pronounced in smaller devices.**

- **Result is V_{TH} depends on channel length (the "reverse short channel effect" only recently understood.**