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Fall 2008 EE 410/510: Microfabrication and Semiconductor Processes

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EB 239 Engineering Bldg.

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Tables and Charts taken from Cambell, Science and Engineering of Microelectronic Fabrication, Oxford 2001
And Wolf and Tauber, Introduction to Silicon Processing for the VLSI Era, Vol. II

Fick's Laws of Diffusion

- Fick's 1st law

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

  - Accurately describes diffusion
  - No convenient measure of current density

- Fick's 2nd law
  - Combines first law with continuity equation

$$-A(J_2 - J_1) = -Adx\frac{\partial J}{\partial x} = Adx\frac{\partial C}{\partial t}$$

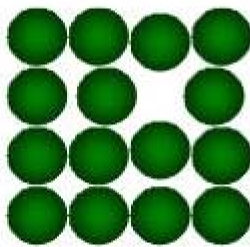
  - Yields concentration over time as a function of second derivative of the concentration gradient through the diffusion constant

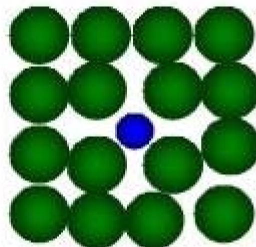
$$\frac{\partial C}{\partial t} = D\nabla^2 C$$

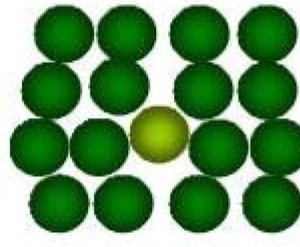
  - Solution requires knowledge of at least two boundary conditions

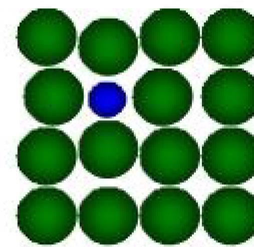
Understanding Atomistic Diffusion

- Physical Mechanisms of Diffusion
  - To use Fick's second law, we must assume that the crystal is isotropic
  - Assumption breaks down when the concentration of the dopant is large
  - At large concentrations, diffusivity becomes a function of concentration and therefore depth.
- Interstitial and substitution diffusion
  - Assume atoms are correctly represented as minima in parabolic potential wells .
  - These atoms are oscillate slightly due to thermal excitation
  - An inserted impurity atom may then sit between lattice sites interstitially.


Vacancy


Interstitial impurity


Self-interstitial


Substitution impurity

Understanding Atomistic Diffusion

- Interstitial and substitution diffusion
  - These impurities diffuse rapidly due to the sharp localized changes in potential energy and do not contribute to doping
  - Diffusion, however allows the impurity to move into an empty lattice site, thereby substituting for its potential into the lattice in place of the matrix material
  - Vacancies filled by substitution remain within the lattice site until sufficient energy is provided for the impurity to move to another empty lattice site. This is achieved by charge redistribution to minimize the free energy of the lattice
  - Vacancies are very dilute in semiconductors at typical process conditions
  - Each of the possible sites can be treated as independent entities.
  - The diffusion coefficient then becomes the probability of all possible diffusion coefficients, weighted by the probability of existence

$$D = D_i + \sum_{a=1} \left[\left(\frac{n}{n_i} \right)^a D^{a-} + \left(\frac{p}{n_i} \right)^a D^{a+} \right]$$

Intrinsic Carrier Concentrations

- The intrinsic carrier concentration is

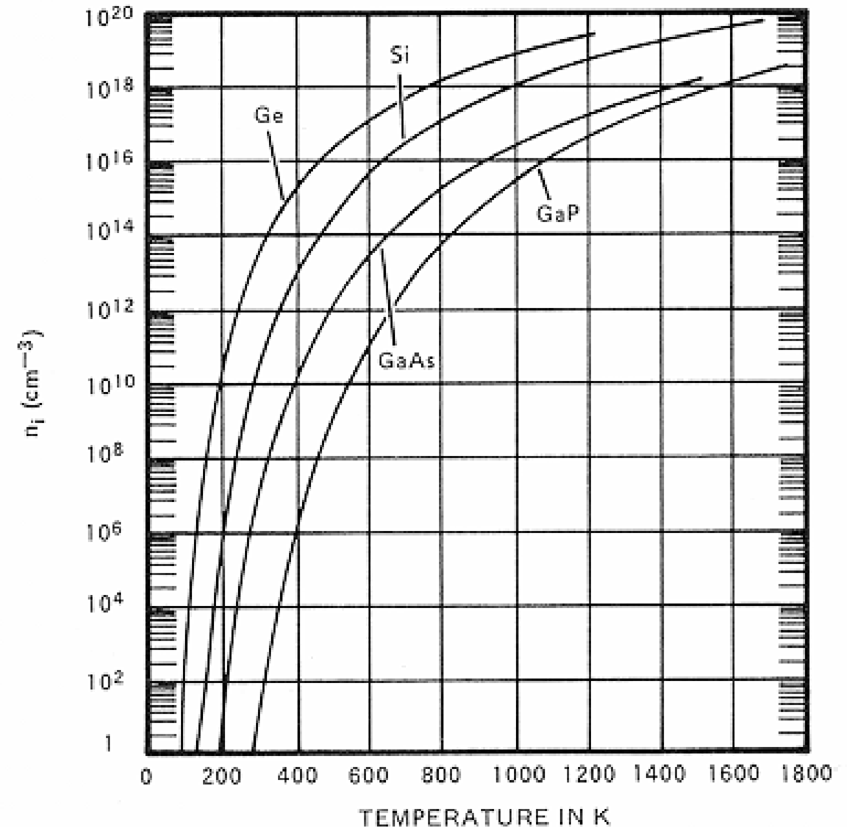
$$n_i(cm^{-3}) = n_{io} T(K)^{3/2} e^{-E_g/(2k_bT)}$$

where n_{io} =7.3*10^{15}cm^{-3} for Si and 4.2*10^{14}cm^{-3} for GaAs

- The bandgap can be determined by

$$E_g = E_{g0} - \frac{\alpha T(K)^2}{\beta + T(K)}$$

where E_{g0}, α, and β are 1.17 eV, 0.000473 eV/K and 636 K for Si and 1.52 eV, 0.000541 eV/K and 204K for GaAs



Understanding Atomistic Diffusion

- In heavily doped silicon, the bandgap is further reduced by the bandgap narrowing effect

$$\Delta E_g = 7.1 * 10^{-10} eV \sqrt{\frac{n(cm^{-3})}{T(K)}}$$

- For heavily doped diffusions ($C >> n_i$) the electron or hole concentration is just the impurity concentration
- For low concentration diffusions ($C << n_i$), n n_i
- For substrates with excess free electrons, the D^+ terms in the diffusion constant are neglected
- For substrates with excess holes, the D^- terms are neglected
- If charged vacancies must be considered, the electron or hole concentration and therefore the diffusivity, is a function of position and Fick's second law must be solved numerically as

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

Understanding Atomistic Diffusion

- If very dilute impurity profiles are measured before and after diffusion, then diffusion coefficients can be determined.
- Repetition of the procedure over several temperatures provides

$$D_i = D_{i_o} e^{-E_{ia}/(k_b T)}$$

  – Where E_{ia} is the activation energy of the intrinsic diffusivity
  – D_{io} is a nearly temperature independent term that depends on vibrational energy and geometry of the lattice

		Donors (D)				Acceptors (A)				
		D_{io}	E_{ia}	D_o^+	E_a^+	D_{io}	E_{ia}	D_o^+	E_a^+	
As in Si	D		12	4.05		0.066		3.44		
P in Si	D	44	4.37	4.4	4	3.9	3.66			
Sb in Si	D		15	4.08		0.21		3.65		
B in Si	A					0.037		3.46	0.41	3.36
Al in Si	A					1.39		4.41	2480	4.2
Ga in Si	A					0.37		3.39	28.5	3.92
S in GaAs	D					0.019		2.6		
Se in GaAs	D					3000		4.16		
Be in GaAs	A					7E-6		1.2		
Ga in GaAs	I					0.1		3.2		
As in GaAs	I					0.7		5.6		

I is interstitial

Analytic Solution of Fick's 2nd Law: (Constant Source)

- In practice, dopant profiles area sufficiently complex and the assumption that the coefficient of diffusion is constant is questionable, thus numerical solutions are generally required
- However rough approximations can be made using analytic solutions
- Solutions are provided for two theoretical conditions
- 1st : Predeposition Diffusion: source concentration (C_s) is fixed for all times, t > 0

$$\frac{\partial C}{\partial t} = D\nabla^2 C$$ Fick's 2nd Law in 1-D

$$C(z,0) = 0$$
$$C(o,t) = C_s$$
$$C(\infty,t) = 0$$

Boundary Conditions

$$C(z,t) = C_s efrc\left(\frac{z}{2\sqrt{Dt}}\right)$$, t > 0 Solution

Estimation of Diffusion profiles

- Dose of predeposition profiles varies with the time of diffusion
- Dose can be obtained using

$$Q_T(t) = \int_0^\infty C(z,t)\,dz = \frac{2}{\sqrt{\pi}} C(0,t)\sqrt{Dt}$$

measured in impurities per unity area (cm^{-2})

- The depth of the profile is typically less than 1 μm
- Dose of 10^{15} cm^{-2} will produce a large volume concentration (>10^{19} cm^{-3})
- Since the surface concentration (C_s) is fixed for a predeposition diffusion, the total dose increases as the square root of time

Analytic Solution of Fick's 2nd Law: (Constant Dose)

- 2st approach: Drive Diffusion: Initial amount of impurity (Q_T) is introduced into the lattice

$$\frac{\partial C}{\partial t} = D\nabla^2 C$$

Fick's 2nd Law in 1-D

$$C(z,0) = 0$$

z . 0

$$\frac{\partial C(o,t)}{\partial z} = 0$$

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

Boundary Conditions

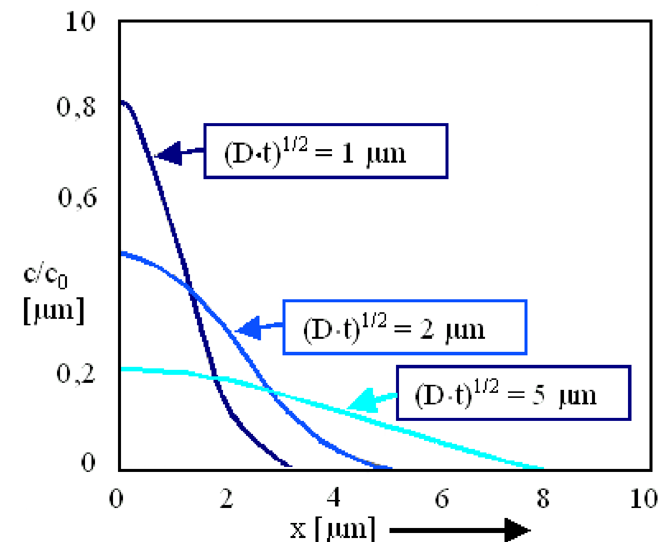
$$\int_0^\infty C(z,t)dz = Q_T$$

Q_T = constant

$$C(z,t) = \frac{Q_T}{\sqrt{\pi D t}} e^{-z^2/(4Dt)}$$

t > 0

Solution



Analytic Solution of Fick's 2nd Law: (Constant Dose)

- With dose is constant, surface concentration must decrease with time:

$$C_s = C(0,t) = \frac{Q_T}{\sqrt{\pi D t}}$$

  - At x = 0, dC/dz is zero for all t 0.
- One classic real world example of these two solutions is a predeposition surface followed by drive in diffusion
  - Recall that the boundary condition for drive in was that the initial impurity concentration was zero everywhere except at the surface
  - Thus drive in is a good approximation for diffusion provided that

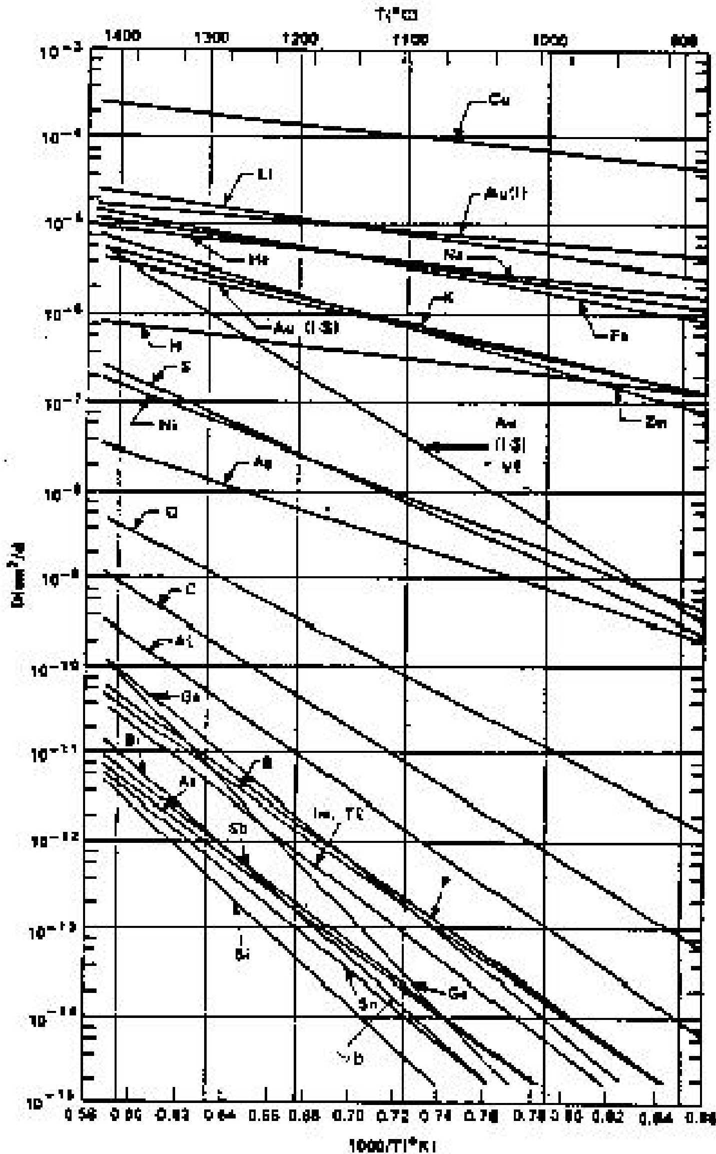
$$\sqrt{Dt_{predep}} << \sqrt{Dt_{drivein}}$$

- Boron (B) is diffusing into Si that as a uniform composition of phosphorus (P), $C_{B.}$
  - Also assume that $C_S >> C_B$
  - A depth will exist at which $C_S = C_B$
  - Since B is p-type and P is n-type, a p-n junction will exist at this depth, x_j:

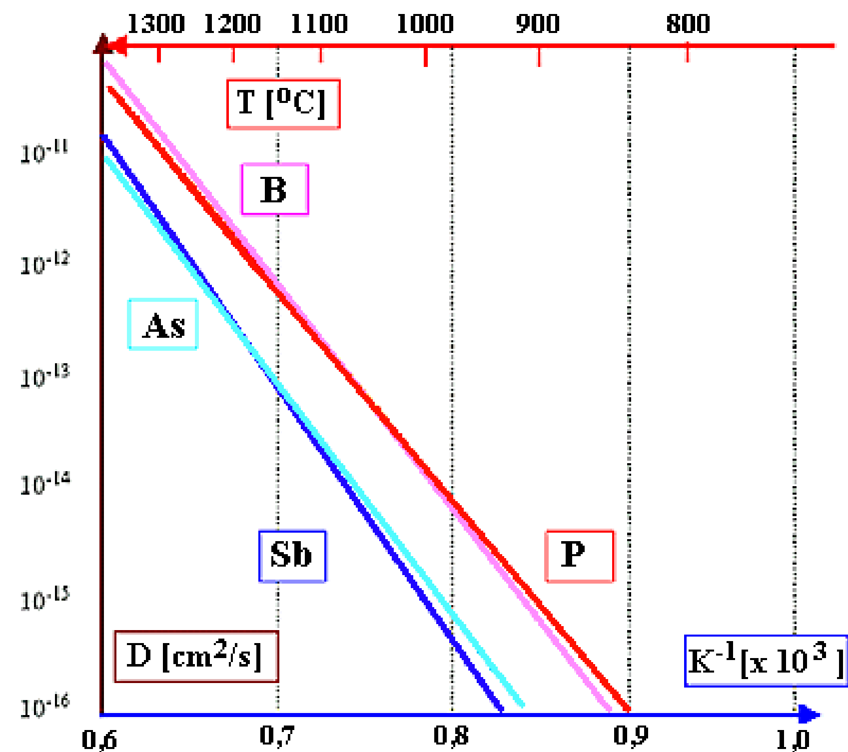
$$x_j = \sqrt{4Dt \ln\left[\frac{Q_T}{C_B\sqrt{\pi D t}}\right]}$$ Drive in

$$x_j = 2\sqrt{Dt}\, efrc^{-1}\left[\frac{C_B}{C_S}\right]$$ Predep

Diffusion of Various Dopants in Si



Online Thermal Diffusion Calculator:
http://www.ece.gatech.edu/research/labs/vc/calculators/DiffCalc.html



Corrections to Simple Theory

- Substitutional impurities are almost completely ionized at room temperature
- Thus an electric field always exist within the substrate
- Total current due to the field effects both drift and diffusion components
- Recalling Ohm's Law:

$$J = -D\frac{\partial C}{\partial z} + \mu C E_x$$

Where μ is the mobility, E is the electric field, and the Einstein relationship between mobility and diffusivity as been invoked.

- Assuming that the carrier concentration is completely determined by the doping profile, then the field can be calculated directly

$$E = -\eta \frac{k_B T}{q}\frac{1}{C}\frac{dC}{dZ}$$

Where η is the screening factor varying from 0 to 1.

$$J = -D(1+\eta)\frac{dC}{dZ}$$

Corrections for Doping under Oxides and Nitrides

- For (C_{doping} >> n_i, C_{Sub}), the profiles own electric filed will enhance movement of the impurity
- Note that the equation is identical to Fick's first law with the slight modification of the screening factor multiplier
- Comparison of inert, oxidizing, and nitridizing dopant diffusion experiments has provided the following conclusions:
  - Diffusion of impurities depends directly on the concentration of impurities
  - Oxidized semiconductors produce a high concentration of excess interstitials at the oxide semiconductor interface
  - Interstitial concentration decays with depth due to recombination
  - Near surface, these interstitials increase the diffusivity of B and P
    - Therefore it is believed that B and P impurities diffuse primarily interstitially
  - Arsenic is diffusivity is found to decrease under oxidized conditions
    - Excess interstitial concentration is expected to decrease local vacancy concentration, therefore, arsenic is primarily believed to diffuse through vacancy mechanisms (at least in oxidized systems)
  - These results have been confirmed by using nitride silicon surfaces which are dominated primarily by vacancies and **NOT** interstitials.
- Dopant diffusivities under oxidizing conditions

$$D = Di + \Delta D = Di + \alpha \left[\frac{dt_{ox}}{dt} \right]^n$$

Where the exponent n has been found experimentally to range from 0.3-0.6 and the α term is (+) for oxidation and (-) for nitridation

High Concentration Doping

- At high concentrations, field enhancement is evident

Arsenic

$$D_{As} \approx 2\frac{n}{n_i}\left(D_i\right)_{As}$$

Phosphorous

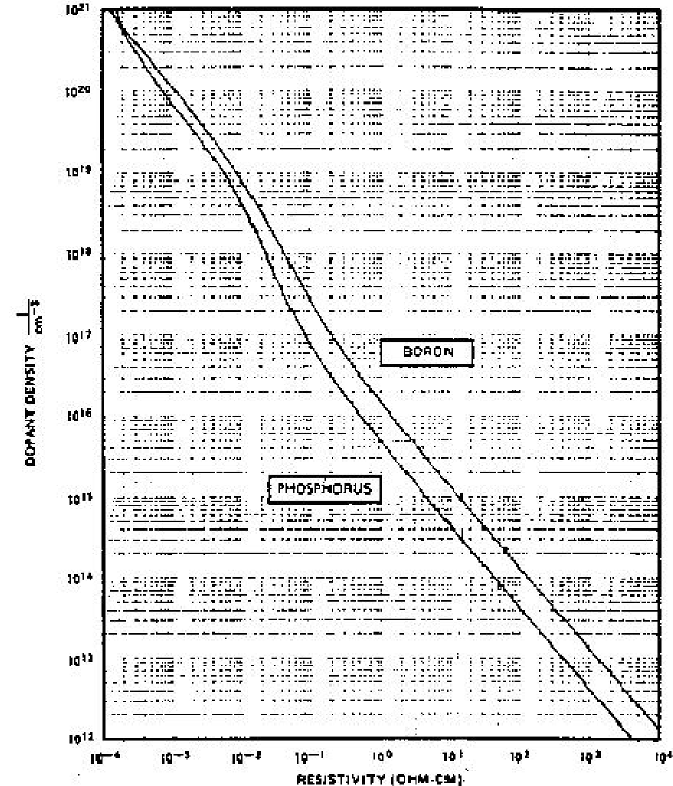
$$D_{Ph} \approx D_i + \left(\frac{n}{n_i}\right)^2 \left(D_i^-\right)$$

- This leads to maximum carrier concentrations of

$$D_{tail} = D_i + D_i^-$$

4 Probe Analysis of Diffused Profiles

- 4 probe Resistance measurement
- Sheet carrier concentration can also be combined with a measurement of junction depth to provide a complete description of the diffused profile
- $C_e(z)$ is the carrier concentration
- $\mu(C)$ is the concentration dependent mobility



$$R = \frac{1}{4}\left[\frac{V_{12}}{I_{34}} + \frac{V_{23}}{I_{41}} + \frac{V_{34}}{I_{12}} + \frac{V_{41}}{I_{23}}\right]$$

$$Rsq = \frac{\pi}{\ln(2)}\frac{1}{R}$$

$$Rsq = \left[q\int \mu(C)C_{e(z)}dz\right]^{-1}$$

Recall from before:

$$Q_T(t) = \int_0^\infty C(z,t)dz = \frac{2}{\sqrt{\pi}}C(0,t)\sqrt{Dt}$$

Hall effect Analsysis of Diffused Profiles

$$\vec{F} = q\vec{v} \times \vec{B}$$ Lorentz Force

$$E_y = v_x B_z$$

$$V_h = v_x B_z w$$

$$v_x = \frac{I_x}{qwx_j \overline{C}_e}$$ Hall Voltage

$$\overline{C}_e = \frac{1}{x_j} \int_0^{x_j} C_e Dx$$ integrated carrier concentration

$$\int_0^{X_j} C_e Dx = \overline{C}_e x_j = \frac{I_x B_x}{qV_h}$$

$$\mu = \frac{1}{qx_j \overline{C}_e R_s}$$ Hall mobility (for epitaxy considerations)