

Doping and diffusion I

Faster MOSFET requires shorter channel

Shorter channel length; yes, but same source & drain depth means drain field dominates gate field
=> "drain-induced barrier lowering" DIBL

Motivation

Requires shallower source, drain

Shallower source, drain depth demands better control in doping & diffusion.
CHANNEL ASPECT RATIO => ρ_s

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How are shallow doped layers made?

- 1) **Predeposition:** controlled number of dopant species at surface
 - '60s: film or gas phase of dopant at surface
 - Surface concentration is limited by equilibrium solubility
 - Now: Ion implant (non-equilibrium), heat substrate to diffuse dopant but ions damage target...requires anneal, changes doping, $c(z)$
 - Soon: return to film or gas phase of dopant at surface
- 2) **Drive-in process:** heat substrate after predeposition, diffusion determines junction depth, sharpness

Need sharper diffusion profiles:

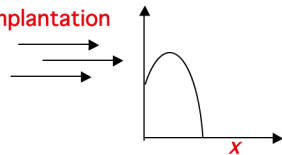
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Pre-deposition & diffusion apparatus

Figure removed for copyright reasons.

Please see: Figures 4.26-4.28 in Ghandi, S. *VLSI Fabrication Principles: Silicon and Gallium Arsenide*. 2nd ed. New York, NY: Wiley-Interscience, 1994. ISBN: 0471580058.

Later...
Ion implantation



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Concept of Diffusion

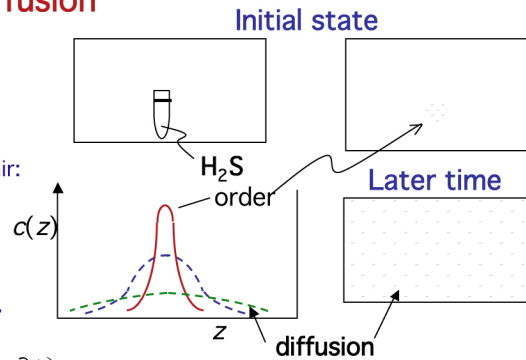
a) Gas diffusion

$$F = U - TS.$$

If no chem'l interaction with air:

$$F = -TS$$

Gas disperses, fills all possible states randomly.

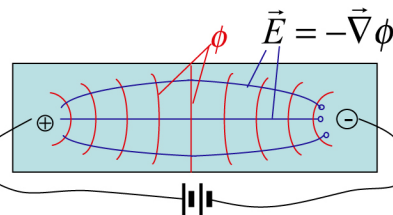


b) $I = \frac{V}{R}$ $J = \sigma E = \sigma \left(-\frac{\partial \phi}{\partial z} \right)$

Electric potential gradient
⇒ charge flow

Electrons drift down potential gradient:

here ϕ is imposed from outside



what about solids...

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c) Mass (or heat) flow J ,
 due to **concentration** gradient

$$J(\#/\text{area} \cdot t) = D \left(-\frac{\partial c}{\partial z} \right)$$

Fick I

d)

$$\frac{dC(z)}{dt} \Delta z = +J(z) - J(z + \Delta z) \frac{\#}{\text{area} \cdot t}$$

$$\frac{dC}{dt} = \frac{J(z) - J(z + \Delta z)}{\Delta z} \xrightarrow{\Delta z \rightarrow 0} -\frac{dJ}{dz}$$

$$\frac{dC(z)}{dt} = -\frac{d}{dz} D \left(-\frac{\partial C}{\partial z} \right) \quad \text{Fick II}$$

...or if D is constant $\frac{dC(z,t)}{dt} = D \nabla^2 C(z,t)$

Time dep. Schrödinger Eq.

$$+i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi$$

These Eqs => time evolution of some initial conditions & boundary conditions

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Atomistic picture of diffusion in solids

See web site for movies:
http://www.tf.uni-kiel.de/matwis/amat/def_en/index.html

Most important is **vacancy diffusion**.

Initial and final states have same energy

Also possible is **direct exchange** (x = broken bond)

Higher energy barrier or break more bonds => lower value of $D = D_0 \exp(-E/kT)$

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Atomistic picture of vacancy diffusion

2 steps
for diffusion: 1) create vacancy 2) achieve energy E_a

$$n_v = \frac{N_v}{N_0} = \exp\left[-\frac{2.6}{kT}\right]$$

$$v_v = v_0 \exp\left(-\frac{E_a}{kT}\right)$$

$$D \sim a \times v = \underbrace{a^2 v_0}_{\left(\frac{\text{cm}^2}{\text{s}}\right)} \exp\left[-\frac{E_v + E_a}{kT}\right]$$

Vacancy diffusion

$D = D_0 \exp\left[-\frac{E_{VD}}{kT}\right]$

Contains $v_0 \approx$ Debye frequency

$$\approx \frac{3 k_B T}{2 h} = 9 \times 10^{12} \text{s}^{-1} \approx 10^{13} \text{s}^{-1}$$

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Solubility limits

From phase diagram:

Sample phase diagram

1.0 T/T_m

Liquid

Liq + Sol

Solid

Solubility dopant in Si

Si at% dopant

1.0 T/T_m

B As P

10^{20} 10^{21}

Impurity content (cm^{-3})

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Solubility limits

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Please see: Figure 2-4 in Campbell, S. *The Science and Engineering of Microelectronic Fabrication*. 1st ed. New York, NY: Oxford University Press, 1996. ISBN: 0195105087.

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Analytic Solution to Diffusion Equations,

Fick II:

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

There are many different solutions to this or any DE;
the correct solution is the one that satisfies the BC.

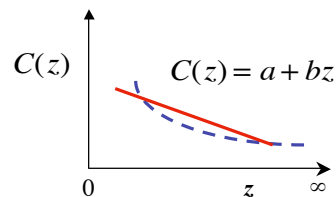
Steady state, $dc/dt = 0$

Implies either a) $D = 0$

$c(z)$ may be curved

or b) $d^2c/dz^2 = 0$

$c(x)$ linear



In oxidation we assumed steady state :

O_2 diffusion through SiO_2 , where

flux $J = -D \frac{\partial C}{\partial z} = -Db$, is same everywhere.

Not necessarily so in diffusion where

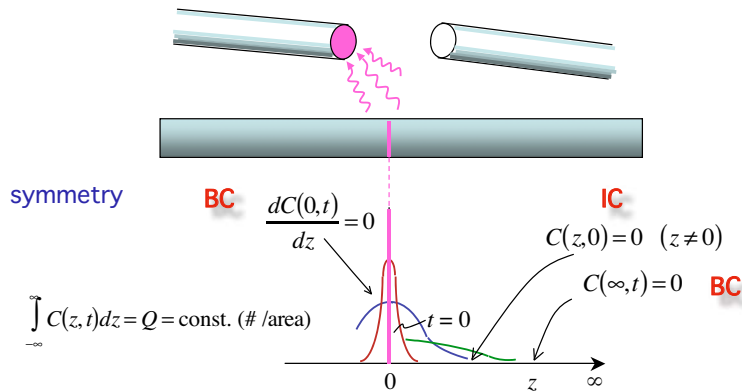
non-linear $c(z)$ can exist and be frozen in at $D = 0$

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For solutions, boundary condition, consider classical experiment:

Diffusion couple: thin *dopant layer* on rod face,
press 2 identical pieces together, heat.
Then study diffusion profile in sections.



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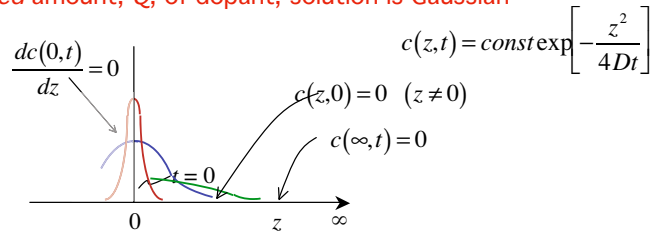
Analytic Solution to Diffusion Equations

$$J = -D \frac{\partial c}{\partial z}$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2}$$

I. "Drive in" of fixed amount, Q , of dopant; solution is Gaussian

Predeposition is delta function, $\delta(z)$.



Dose, Q , amount of dopant in sample, is constant. $\int_{-\infty}^{\infty} C(z,t) dz = Q = \text{const.} \text{ (#/area)}$

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

Units
#/vol = $Q/(\text{length}^2)^{1/2}$
So Q has units #/area

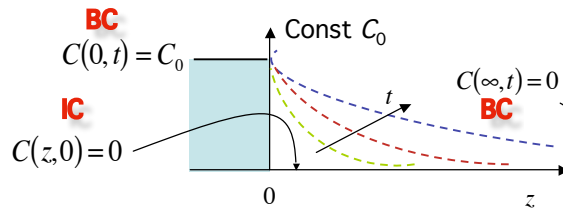
$\frac{1}{2}$ Width of Gaussian = $a = 2\sqrt{Dt}$ = diffusion length a
(a is large relative to width of predeposition)

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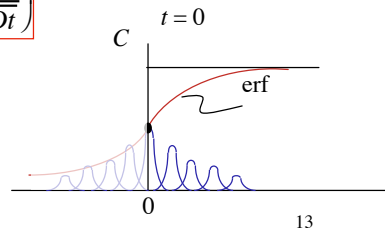
Solutions for other I.C./B.C. can be obtained by superposition:

II. *Limitless* source
of dopant
(e.g. growth in
presence of vapor)



$$C_{\text{imp}}(z, t) = \frac{2}{\sqrt{\pi}} \int_0^{\frac{z}{2\sqrt{Dt}}} \exp[-\xi^2] d\xi \equiv \text{erf}(u) = \text{erf}\left(\frac{z}{2\sqrt{Dt}}\right)$$

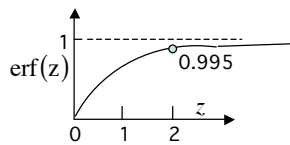
$$\xi^2 = \frac{z^2}{4Dt} \rightarrow \frac{(z - z_0)^2}{4Dt}$$



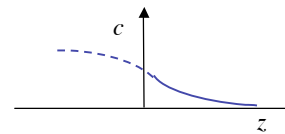
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Other I.C./B.C. (cont.):



$$\text{erfc}(u) = 1 - \text{erf}(u)$$



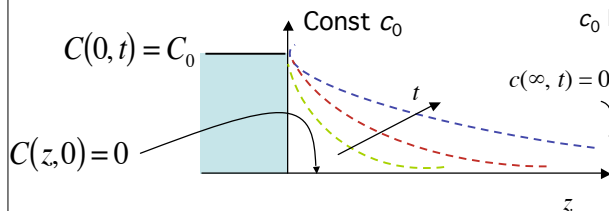
$$C(z, t) = C_{\text{surf}} \text{erfc}\left[\frac{z}{2\sqrt{Dt}}\right], \quad t > 0$$

$$a = \text{diffusion length} = 2\sqrt{Dt}$$

$$(D \approx 10^{-15}) \times (t = 10^3) \Rightarrow a \approx 0.2 \mu\text{m}$$

$$\text{Dose} \equiv Q = \int_0^{\infty} C(z, t) dz = \frac{2\sqrt{Dt}}{\sqrt{\pi}} C_0 = \frac{a}{\sqrt{\pi}} C_0$$

c_0 limited by solid solubility



Dose, Q,
amount of dopant
in sample,
increases as $t^{1/2}$.

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$$\frac{dC(z)}{dt} = -\frac{d}{dz} D \left(-\frac{\partial C}{\partial z} \right) \quad \text{Fick II}$$

...or if D is constant $\frac{dC(z,t)}{dt} = D \nabla^2 C(z,t)$

Time evolution of some initial conditions & boundary conditions

IC $c(z, t = 0) = 0$

BCs $c(\infty, t) = 0$
 $c(0, t) = c_0$

IC $c(z \neq 0, t = 0) = 0$

BCs $c(\infty, t) = 0$
 $\nabla c(0, t) = 0$

IC $c(z \neq z_0, t = 0) = 0$

BCs $c(\infty, t) = 0$
 $\nabla c(z_0, t) = 0$

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But measured diffusion profiles are rarely as simple as Gaussian or erfc:

Note:
Log(erfc)
& Log(gaussian)
look more alike than non-Logs

Figure removed for copyright reasons.

Please see: Figure 7-28 in Plummer, J., M. Deal, and P. Griffin. *Silicon VLSI Technology: Fundamentals, Practice, and Modeling*. Upper Saddle River, NJ: Prentice Hall, 2000. ISBN: 0130850373.

Why is diffusion enhanced at high concentration?

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Internal E fields alter Fick's Law

Heavily doped layer can generate its own field
due to displacement of mobile carriers from ionized dopants:

p-type Si

E enhances diffusion of A^- to right, (also down concentration gradient).

$$J_{\text{mass}} = -D \frac{\partial C}{\partial z} + C \mu \bar{E} \equiv D \left[-\frac{\partial C}{\partial z} + \frac{C q \bar{E}}{kT} \right]$$

$\xrightarrow{\text{diffusion}}$ $\xrightarrow{A^- \text{ drift}}$

$\left[\mu = \frac{Dq}{kT} \right]$
Einstein relation from Brownian motion
 (units)

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Neutral and charged impurities, dopants

If impurity is Gp. IV (e.g. Ge): uncharged, no e or h

But if impurity = B, P As... it will be charged:

So vacancies can be charged

For small dopant concentration, different diffusion processes are independent, but generally:

$$D_0 e^{\frac{E_a}{kT}} = D \Rightarrow D^0 + D^{1-} \frac{n}{n_i} + D^{2-} \left(\frac{n}{n_i} \right)^2 + \dots + D^{1+} \left(\frac{p}{p_i} \right) + D^{2+} \left(\frac{p}{p_i} \right)^2 + \dots$$

electrons n_i

(these D^p are NOT same as single activation energy values)

Intrinsic Diffusivities and Activation Energies of Substitutional Diffusers in Silicon*							
		P	As	Sb	B	Al	Ga
D_0^0	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_0^{1-}	D_0	—	—	—	0.76	2480	28.5
	E_0	—	—	—	3.46	4.20	3.92
D_0^{1+}	D_0	4.44	22.9	13	—	—	—
	E_0	4.0	4.1	4.0	—	—	—
D_0^{2-}	D_0	44.2	—	—	—	—	—
	E_0	4.37	—	—	—	—	—

* D_0 in cm^2/s ; E_0 in eV.

Power series representation; higher orders in n describe dopant-dopant interactions

[Higher activation energy for charged vacancy diffusion; prefactor is greater]

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Figure by MIT OCV.

“What is n ?”

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

n is local free electron concentration in host. $n \geq n_i$ always

$$n \approx \frac{N_D}{2} + \sqrt{\left(\frac{N_D}{2}\right)^2 + n_i^2}$$

So clearly, $D^{\text{eff}} = D^0 + D^-(n/n_i) + \dots$ can be $\gg D = D_0 \exp(-E_{VD}/kT)$

(provided D^+ etc not too small)

For intrinsic semiconductor or $N_D \ll n_i$, $n = p = n_i$

See example Plummer, p. 412, As

$$D^{\text{eff}} = D^0 + D^-(1) + \dots$$

$$n_i = 7.14 \times 10^{18} \text{ at } 1000^\circ\text{C}$$

$$D_{\text{As}}^{\text{eff}} = D^0 + D^-(n/n_i) + \dots$$

$$2.67 \times 10^{-16} + 1.17 \times 10^{-15}(n/n_i)$$

$$N_D = 10^{18}: D_{\text{As}}^{\text{eff}} = 1.43 \times 10^{-15}$$

$$N_D = 10^{20}: D_{\text{As}}^{\text{eff}} = 16.6 \times 10^{-15}$$

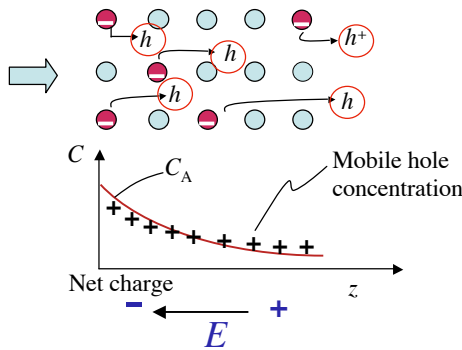
Caution: these numbers not from table on prior slide

(Single-activation-energy value: $D = 1.5 \times 10^{-15}$)

Internal E field

Is related to

concentration dependent diffusion



$$D^{\text{eff}} = D^0 + D^-\left(\frac{n}{n_i}\right) + D^{2-}\left(\frac{n}{n_i}\right)^2 + \dots$$

Higher dopant concentration means greater charge separation, Δq , thus larger internal electric fields.

E enhances diffusion of A^- to right, (also down concentration gradient).

Exercise

Calculate diffusivity of P in Si at 1000° C for

- a) $c_p < n_i$ b) $c_p = 4 \times 10^{19} \text{ cm}^{-3}$
- c) compare diffusion length b) with uncharged estimate

a) $c_p < n_i = 10^{19}$
 from Fig 1.16

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Please see: Figure 1.16 in Plummer et al., 2000.

Exercise

Calculate diffusivity of P in Si at 1000° C for

- a) $c_p < n_i$ b) $c_p = 4 \times 10^{19} \text{ cm}^{-3}$
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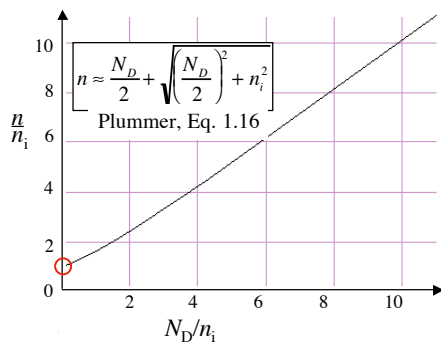
a) $c_p < n_i = 10^{19}$

Diffusion of P in Si			
D_0	E_a	D_0^-	E_a^-
(cm^2/s)	(eV)	(cm^2/s)	(eV)
3.85	3.66	4.4	4.0

$$D_p^0 = 3.85 \exp\left[-\frac{3.66}{kT}\right] = 1.3 \times 10^{-14} (\text{cm}^2 \text{s}^{-1})$$

$$D_p^- = 4.4 \exp\left[-\frac{4}{kT}\right] = 6.63 \times 10^{-16} (\text{cm}^2 \text{s}^{-1})$$

$$D = D_p^0 + D_p^- \left(\frac{n}{n_i}\right) = 1.37 \times 10^{-14} (\text{cm}^2 \text{s}^{-1})$$



Linear approximation

Single-valued D

Better than single-activation-energy :

$$D_p = 4.7 \exp\left[-\frac{3.68}{kT}\right] = 1.3 \times 10^{-14} (\text{cm}^2 \text{s}^{-1})$$

Exercise

Calculate diffusivity of P in Si at 1000° C for

a) $c_p < n_i$ b) $c_p = 4 \times 10^{19} \text{ cm}^{-3}$

c) compare diffusion length b) with uncharged estimate

$$\text{b) } c_p = N_D = 4 \times 10^{19} \quad n \approx \frac{N_D}{2} + \sqrt{\left(\frac{N_D}{2}\right)^2 + n_i^2} = 2 \times 10^{19} + \sqrt{4 \times 10^{38} + 10^{38}} = 4.24 \times 10^{19} \text{ cm}^{-3}$$

Plummer, Eq. 1.16

$$D = D_p^0 + D_p^- \left(\frac{n}{n_i}\right) = 1.3 \times 10^{-14} + 6.63 \times 10^{-16} \left(\frac{4.24}{1}\right) = 1.57 \times 10^{-14} \text{ (cm}^2 \text{ s}^{-1}\text{)} \quad \text{vs 1.37}$$

$$\text{c) } a = 2\sqrt{Dt}, \quad 1 \text{ hr} \Rightarrow a_0 = 2\sqrt{1.30 \times 10^{-14} \times 3600} = 0.137 \text{ } \mu\text{m}$$

$$a_p = 2\sqrt{1.57 \times 10^{-14} \times 3600} = 0.151 \text{ } \mu\text{m}$$

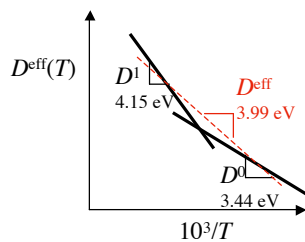
(This is a measure of the depth of doping.)

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Consequence:

Diffusion is enhanced
at high dopant
concentrations,
giving sharper
diffusion profile



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Effect of oxidation of Si on diffusion

Plummer
Fig. 7.36

B and P
observed to diffuse faster
when Si surface is oxidized,
Sb slower. Why?

So far
we have concentrated on
diffusion
by vacancy mechanism

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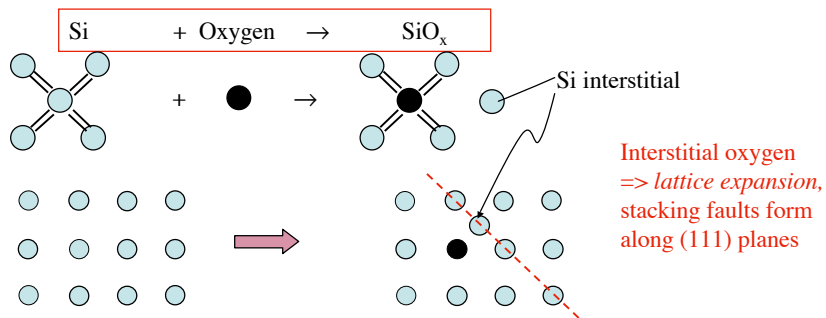
Please see: Figure 7-36 in Plummer et al., 2000.

Different behavior of B and Sb under oxidation suggests
a different mechanism may dominate in these two dopants...

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Effect of surface oxidation on diffusion in Si



Because B and P diffuse mainly by an *interstitial* process;

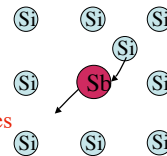
their diffusion is enhanced by oxidation.

But Sb is large and diffuses only by vacancies.

Si interstitials created by oxidation,

recombine and reduce concentration of vacancies

suppressing diffusion of Sb atoms.



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Diffusion process is different for different species.

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Please see: Figure 7-15 in Plummer et al., 2000.

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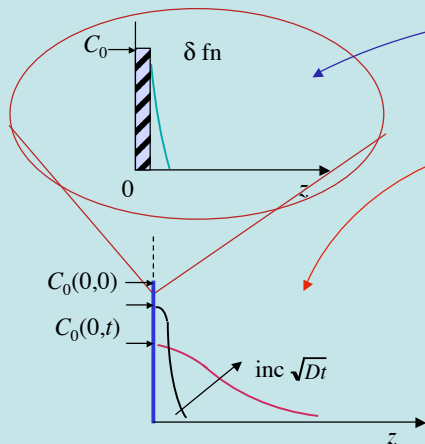
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Review: Doping and diffusion, *small dose*

$$\frac{dC(z,t)}{dt} = \frac{d}{dz} \left(D \frac{dC}{dz} \right)$$

Plus I.C. and B.C.s

If “predeposition” is *small dose*,
followed by a higher T ,
longer t (larger $a \sim \sqrt{Dt}$)
“drive-in” process.



- 1) I.C. $C(z, 0) = 0 \quad z > 0$
- 2) B.C. $C(\infty, t) = 0, \quad dC(0,t)/dz = 0$
- 3) **Fixed** dose $Q = \frac{a}{\sqrt{\pi}} c_0$

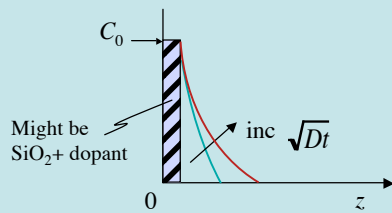
$$C(z,t) = \frac{Q}{\sqrt{\pi Dt}} \exp \left[- \left(\frac{z}{a} \right)^2 \right]$$

$C(0,t) = \frac{Q}{\sqrt{\pi Dt}}$ decreases like $t^{-1/2}$

Review: Doping and diffusion, large dose

Diffusion preceded by “pre-deposition” to deliver a *large amount* of impurity.

If pre-dep is *inexhaustible* or equivalently, if $a \sim \sqrt{Dt}$ is small, then



1) I.C. $C(z, 0) = 0 \quad z > 0$

2) B.C. $C(\infty, t) = 0$

3) B.C. $C(0, t) = C_0$

$$C(z, t) = C_0 \operatorname{erfc} \left[\frac{z}{a} \right] \quad a = 2\sqrt{Dt}$$

$$\text{Dose} \equiv Q = \int_0^\infty C(z, t) dz = \frac{2\sqrt{Dt}}{\sqrt{\pi}} C_0 = \frac{a}{\sqrt{\pi}} C_0$$

C_0 limited by solid solubility

Junctions between different doped regions

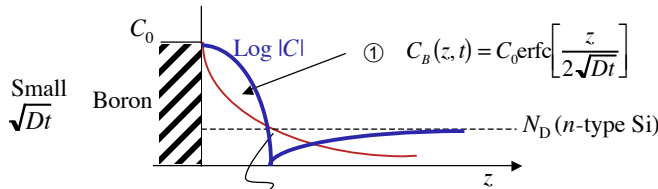
Diffuse B at high concentration, into *n*-type Si, (uniformly doped, N_D , with P).

Want to know depth of *p-n* junction ($N_A = N_D$)

Consider limitless dopant source (i.e. erfc)

boron

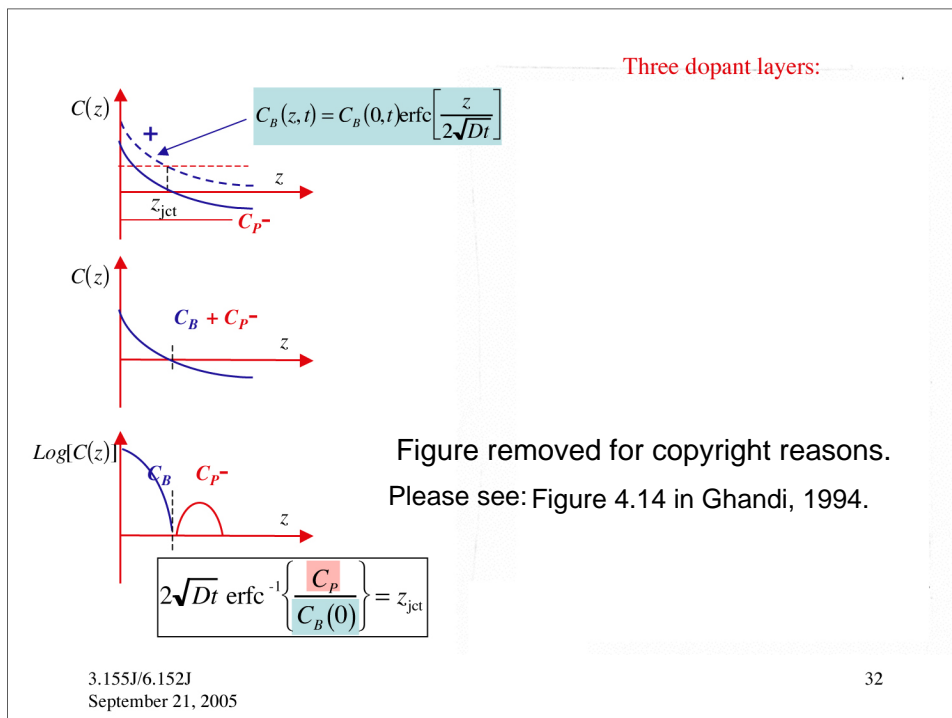
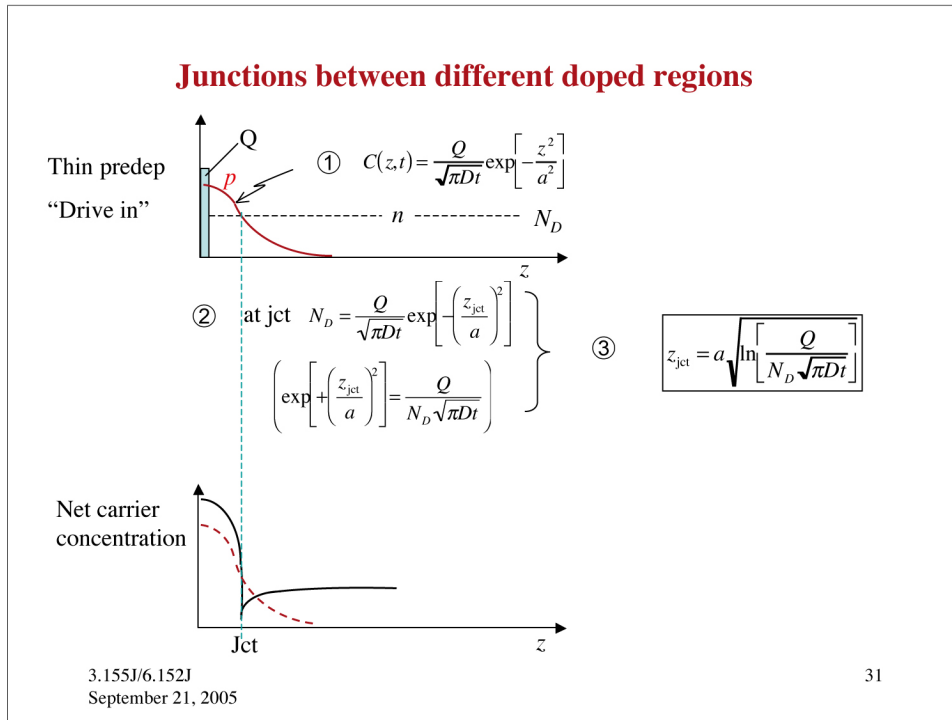
phosphorus



① $C_b(z, t) = C_0 \operatorname{erfc} \left[\frac{z}{2\sqrt{Dt}} \right]$

junction $N_D = C_0 \operatorname{erfc} \left[\frac{z_{\text{jct}}}{a} \right]$ ②

$$z_{\text{jct}} = a \operatorname{erfc}^{-1} \left[\frac{N_D}{C_0} \right] \quad a = 2\sqrt{Dt} \quad \text{③}$$



Internal E fields alter Fick's Law
 D is not a constant, but depends on $c(x)$

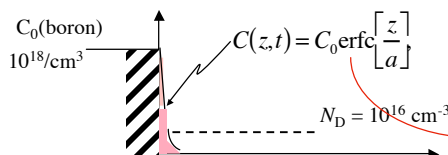
Figure removed for copyright reasons.
 Please see: Figure 7-26 in Plummer et al., 2000.

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Exercise

n -type Si, $N_D = 10^{16} \text{ cm}^{-3}$ is doped with boron
 from a const source with C_0 (boron) = 10^{18} cm^{-3}



Question:

If exposed to c_0 at 1000°C for 1 hr,
 what is junction depth?

$$z_{\text{jct}} = a \operatorname{erfc}^{-1} \left[\frac{N_D}{C_0} \right] = 2\sqrt{Dt} \operatorname{erfc}^{-1} [10^{-2}]$$

Let $\operatorname{erfc}^{-1} [10^{-2}] = x$, $\operatorname{erfc}[x] = 0.01 = 1 - \operatorname{erf}[x]$, $\operatorname{erf}[x] = 0.99$

From appendix, $x = 1.82 = z/[2(Dt)^{1/2}]$

$$D(\text{boron}) = 0.037 \exp \left[-\frac{3.46}{kT} \right] \xrightarrow{1273 \text{ K}} 7.6 \times 10^{-16} \text{ cm}^2/\text{s}$$

$$a = 2\sqrt{Dt} = 3.31 \times 10^{-6} \text{ cm} = 0.033 \mu\text{m}$$

$$z_{\text{jct}} = 0.033 \times 1.82 = 0.06 \mu\text{m}$$

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$z_{jct} = 0.033 \times 1.82 = 0.06 \mu\text{m}$

From $z_{jct}(t)$ and $z_{jct}(0) = 0$,
you can calculate
junction depth
at different time:

Question: Now constant source is removed
and this dose, $C(z, 1\text{hr})$, is “driven in” farther for 1 hr at 1100°C.

Now where is junction?

$$Q = \int C(z, 1\text{hr}) dz = \frac{aC_0}{\sqrt{\pi}} = 1.87 \times 10^{12} \text{cm}^{-2}$$

$$D(\text{boron}) \xrightarrow{1373 \text{ K}} 7.57 \times 10^{-15} \text{cm}^2/\text{s} \quad \sqrt{Dt} = 5.22 \times 10^{-6} \text{cm}$$

$$z_{jct} = a \sqrt{\ln\left(\frac{Q}{N_D \sqrt{\pi Dt}}\right)} = 1.8 \times 10^{-5} \text{cm} = 0.18 \mu\text{m}$$

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Measuring diffusion profiles

Resistance $R = \rho \frac{L}{A} (\Omega)$	resistivity $\rho = \frac{RA}{L} (\Omega\text{m})$	conductivity $\sigma = \frac{1}{\rho} = nq\mu$
---	---	---

But n, μ are functions of position due to doping

$$\langle \sigma \rangle = \frac{q}{t} \int_0^t n(z)\mu(n) dz$$

$$\langle \rho \rangle = \frac{1}{\langle \sigma \rangle} = \frac{t}{q \int n\mu dz}$$

Define

sheet resistance

$$\frac{\rho}{t} \equiv R_s = \frac{RA}{Lt} = R \frac{W}{L} \left(\frac{\Omega}{sq}\right)$$

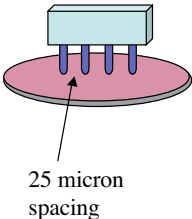
an average measurement of n

Spreading resistance probe:
(Developed at Bell Labs in '40s)

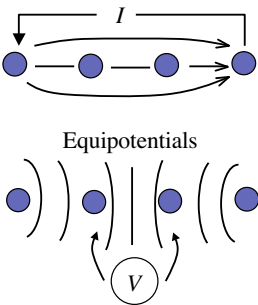
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Measuring diffusion profiles

4-point probe

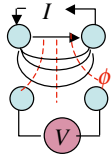


25 micron spacing




Equipotentials

Also square array
(Van der Pauw method)

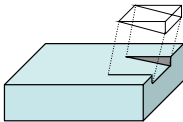


These \Rightarrow average n if done from surface.

These are most useful if done on beveled wafer:



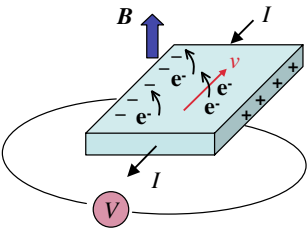
Polish off \Rightarrow depth profile

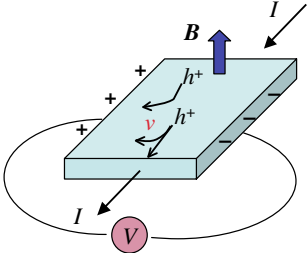


sample

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Hall effect: electrical transport in magnetic field.





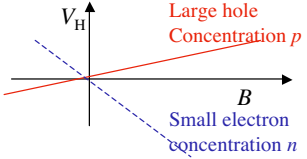
$$F = q\langle v \rangle \times B$$

$$J = nq\langle v \rangle$$

$$\left. \begin{array}{l} F = q\langle v \rangle \times B \\ J = nq\langle v \rangle \end{array} \right\} \frac{F}{q} = E_H = \frac{J}{nq} B \quad \boxed{E_H = R_H (J \times B)}$$

Hall coefficient \Rightarrow charge sign and concentration
 R_H is slope of V vs B data

$R_H = \frac{1}{nq}$



Again an average measurement

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Capacitance

(Secondary ion mass spectroscopy)

RBS

(Rutherford back scattering)

Use MOS structure, gate & substrate are electrodes

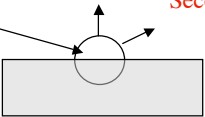
Useful for lightly doped regions

$C = \frac{\epsilon A}{d}$ — Depletion width

Ion source

1 - 5 k eV

Sputters surface

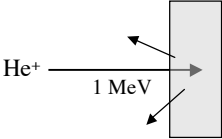


Secondary ions to mass spectrometer

Depth profile

Backscatter energy depends on depth and impurities

Backscatter intensity \propto (mass impurities)²



Ions penetrate

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