Doping and diffusion I   Motivation
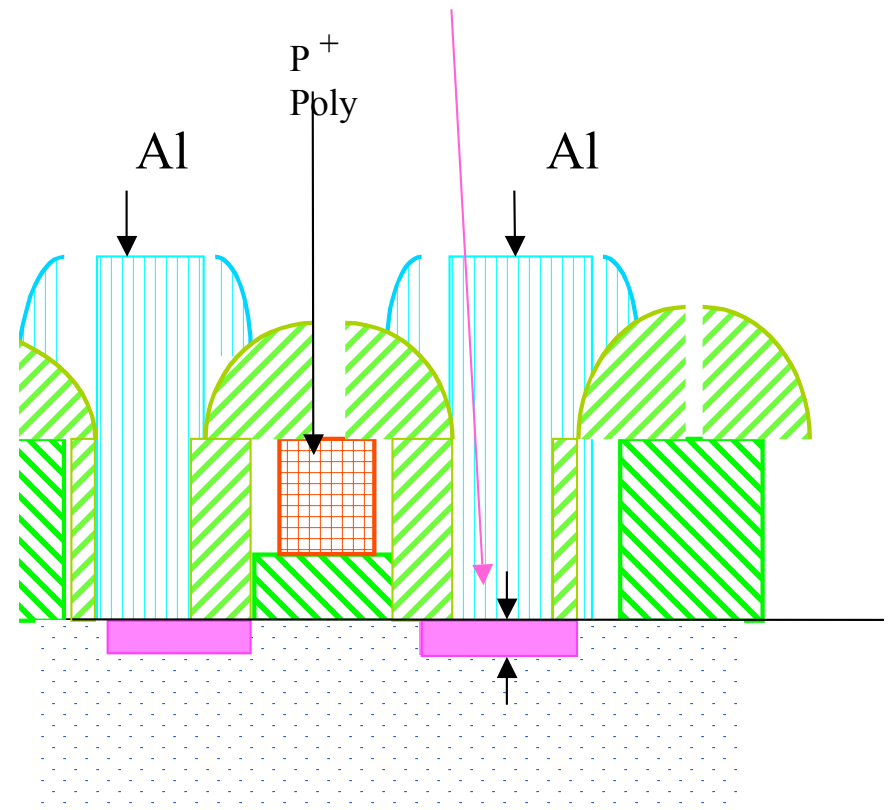
Faster MOSFET requires shorter channel

Requires shallower source, drain

P $^+$ Poly

Al   Al

Al   Al

P $^+$ Poly
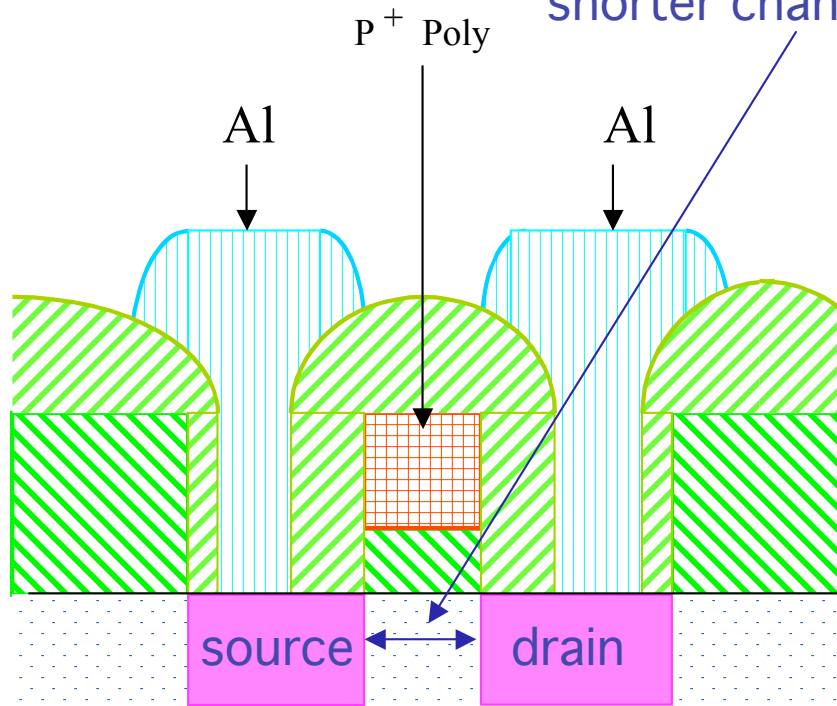
source ⟷ drain

Shorter channel but with
same source, drain depth =>
drain field dominates gate field
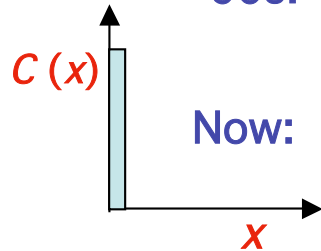 =>"drain-induced barrier lowering" DIBL

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

How are shallow doped layers made?

1) Predeposition: controlled number of dopant species at surface

'60s: film or gas phase of dopant at surface

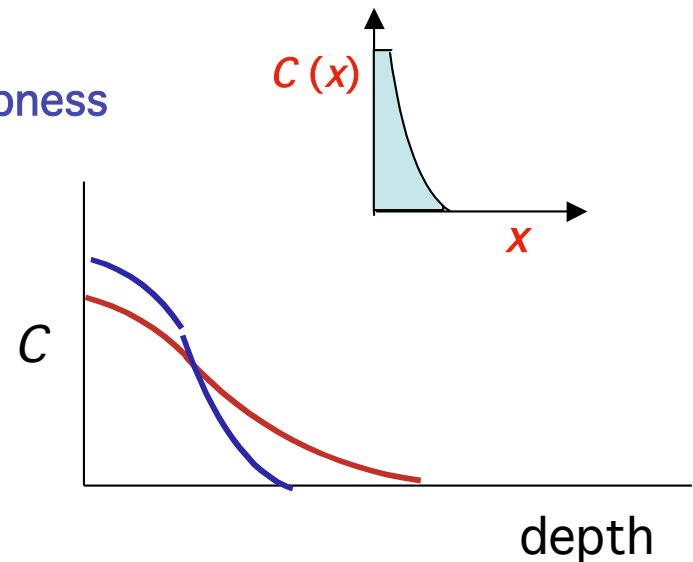$C(x)$ Surface concentration is limited by equilib . solubility

Now: Ion implant (non-equilibrium) , heat substrate to diffuse dopant

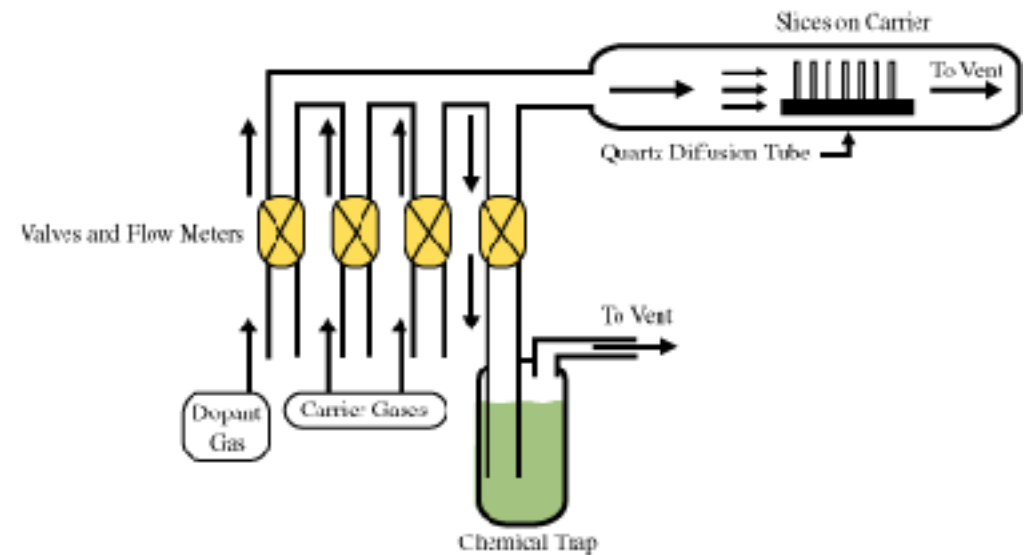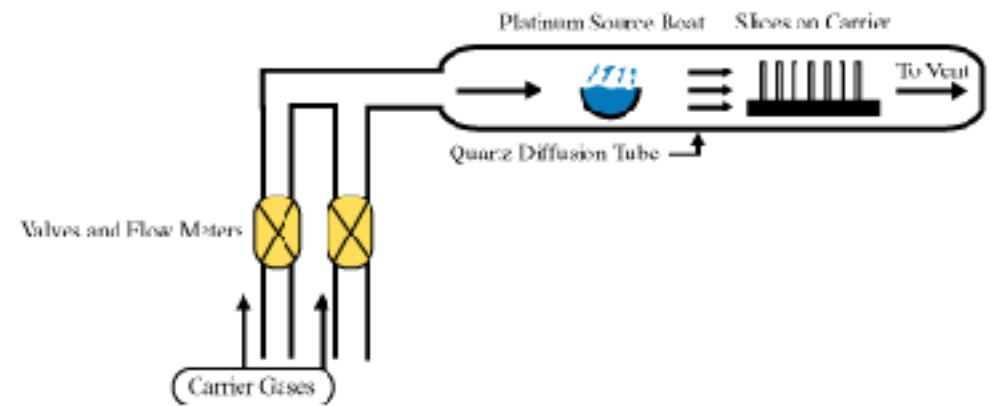but ions damage target...requires anneal, changes doping, $C(z)$

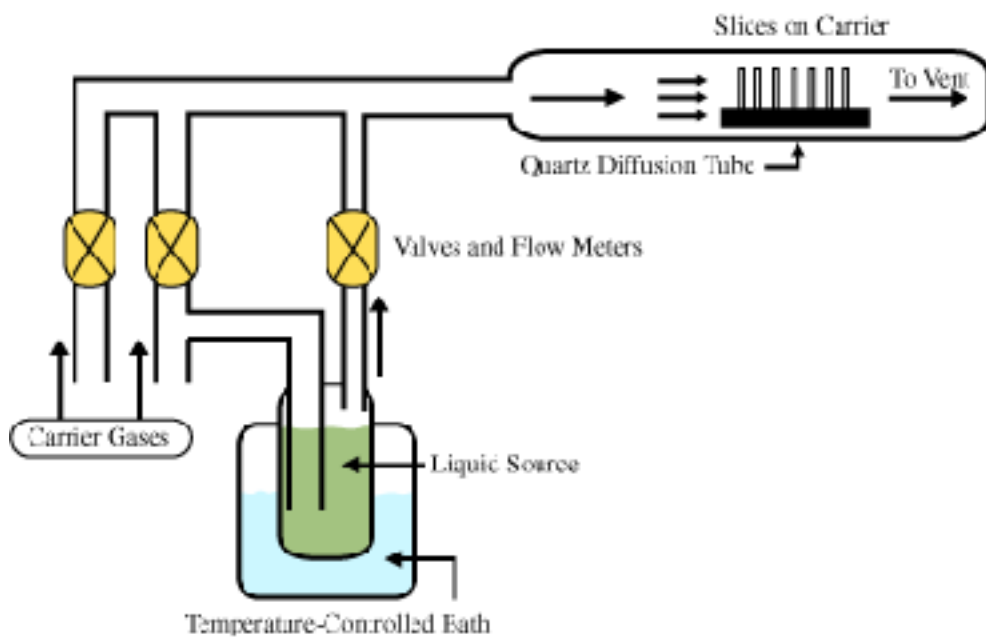Soon: film or gas phase of dopant at surface

x

2) Drive-in process: heat substrate+predep,
diffusion determines junction depth, sharpness

$C(x)$

x

Need
sharper diffusion profiles:

C

depth

Doping and diffusion apparatus

Slices on Carrier

To Vent

Quartz Diffusion Tube

Valves and Flow Meters

Carrier Gases

Liquid Source

Temperature-Controlled Bath

Platinum Source Boat   Slices on Carrier

To Vent

Quartz Diffusion Tube

Valves and Flow Meters

Carrier Gases

Slices on Carrier

To Vent

Quartz Diffusion Tube

Valves and Flow Meters

Dopant Gas   Carrier Gases

To Vent

Chemical Trap

Later...
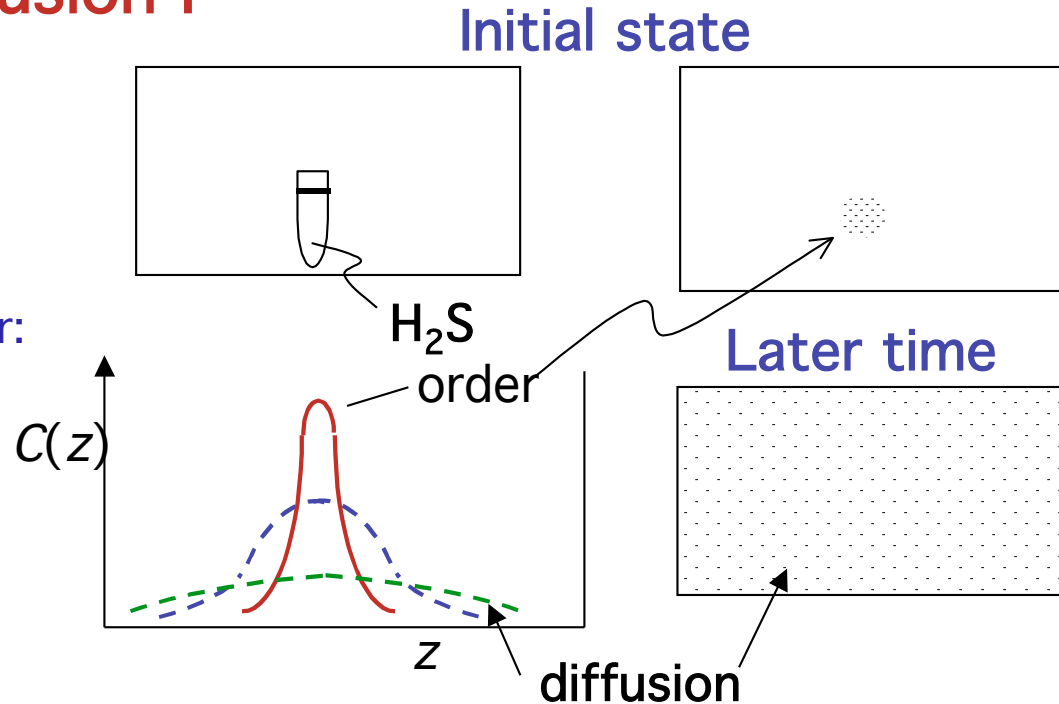**Ion Implantation**

x
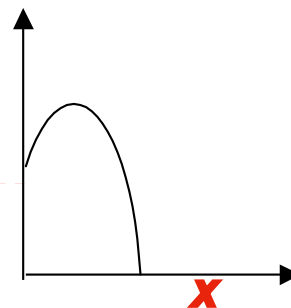
Doping, Diffusion I

Initial state

a) Gas diffusion

$$F = U - TS.$$

If no chem'l interaction with air:

$$F = -TS$$

Gas disperses, fills all possible states randomly.
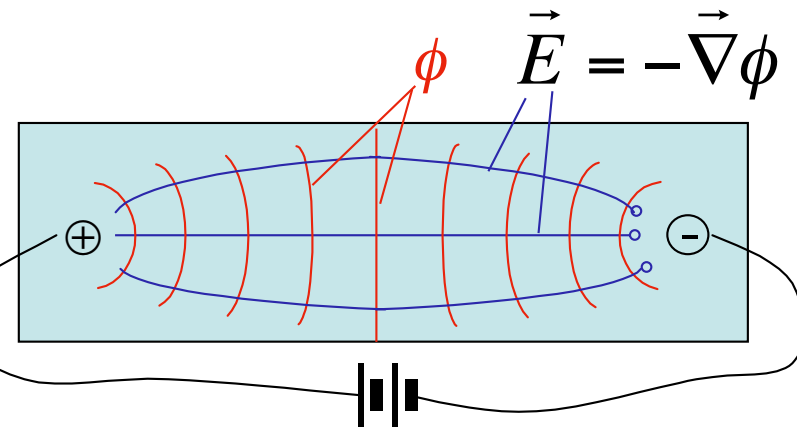
H_2S

order

$C(z)$

Later time

z

diffusion

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

Electric potential gradient

$\Rightarrow$ charge flow

Electrons drift down potential gradient:

here ϕ is imposed from outside
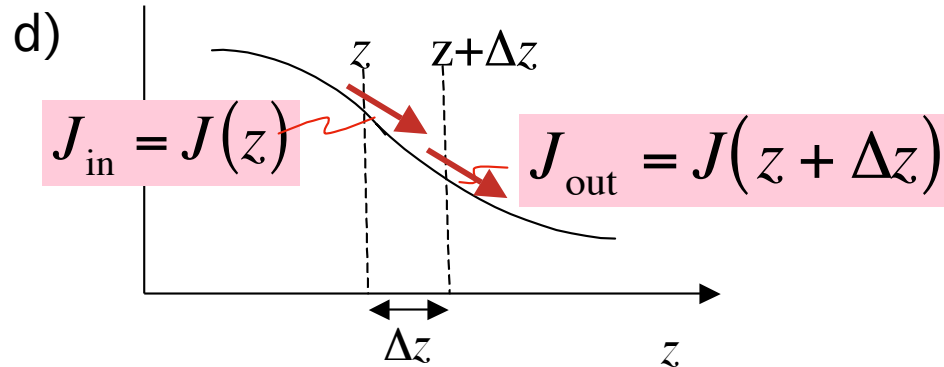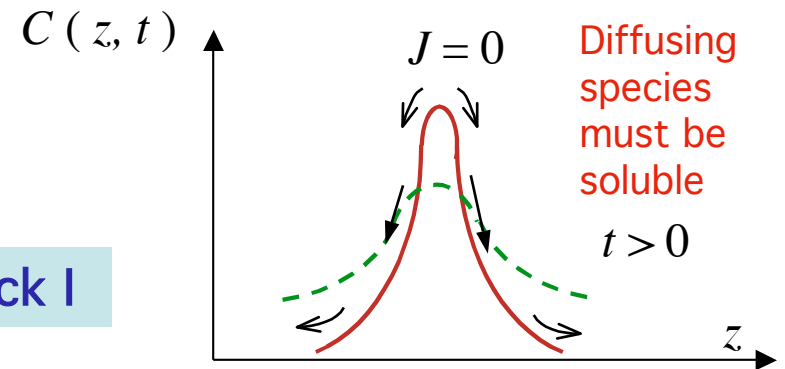
ϕ $\vec{E} = -\vec{\nabla}\phi$

$+$ $-$

what about solids...

c) Mass (or heat) flow J,

due to concentration gradient

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

Fick I

$C(z,t)$

$J = 0$

Diffusing species must be soluble

$t > 0$

z

d)

z $z+\Delta z$

$J_{in} = J(z)$

$J_{out} = J(z + \Delta z)$

Δz z

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

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

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

Fick II

...or if D is constant

$$\frac{dC(z,t)}{dt} = D\nabla^2 C(z,t)$$

Time dep. Schrödinger Eq.

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

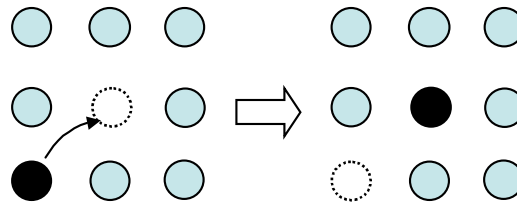These Eqs => time evolution of some initial conditions, boundary conditions

Atomistic picture of diffusion

Most important is **vacancy diffusion.**

En

E_a

i   f
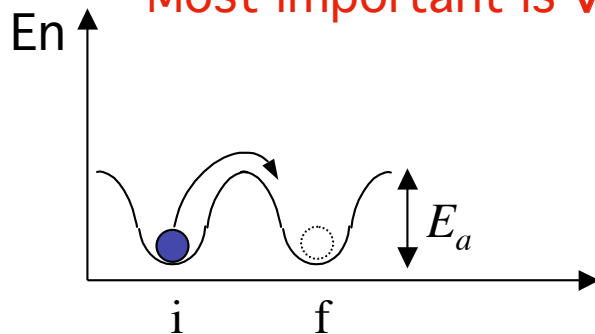
Initial and final states have same energy

Also possible is direct exchange (× = broken bond)
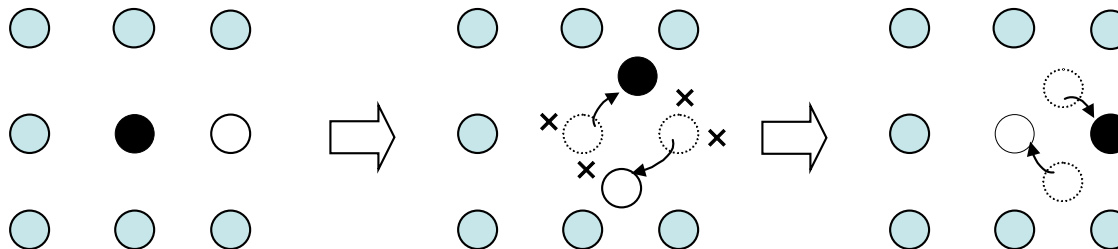
Higher energy barrier or break more bonds => lower value of $D = D_0 \exp\left(-\dfrac{E}{kT}\right)$

Atoms that bond with Si are

substitutional impurities P, B, As, Al, Ga, Sb, Ge

6.155/ 3.155J   9/29/03

7

Atomistic picture of diffusion

2 steps
for diffusion: 1) <u>create vacancy</u>   2) <u>achieve energy E_a</u>

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

$$\nu_v = \nu_0 \exp\left(-\frac{E_a}{kT}\right)$$

$$\left(e^{-\frac{\Delta G}{kT}} \rightarrow e^{-\frac{E_{VF}-TS}{kT}} = e^{\frac{S}{k}} e^{-\frac{E_{VF}}{kT}} \right)$$

$$D \sim a \times \nu = a^2 \nu_0 \underbrace{\exp\left[-\frac{E_v + E_a}{kT}\right]}_{\left(\frac{cm^2}{s}\right)}$$

Vacancy diffusion

ν_0

E_{VD}

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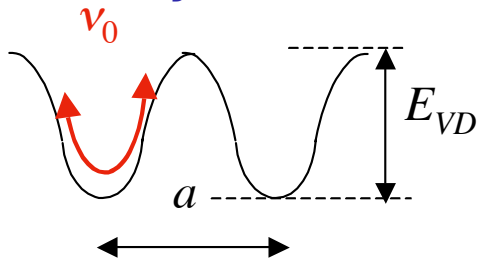
$$\boxed{D = D_0 \exp\left[-\frac{E_{VD}}{kT}\right]}$$

Contains $\nu_0 \approx$ Debye frequency

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

Analytic Solution to Diffusion Equations,

Fick II:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2}$$
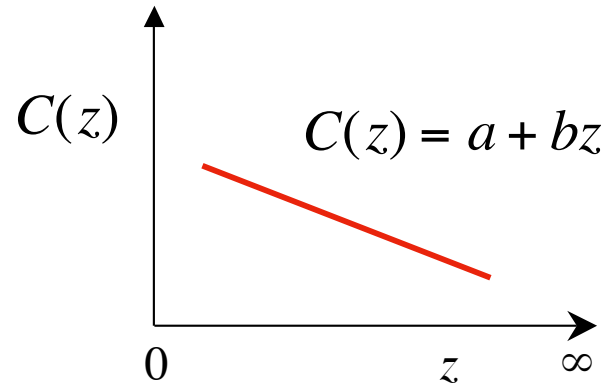
Steady state, $dC/dt = 0$

Conversely,
  if $C(z)$ is curved,
    $dC/dt \neq 0$.

$C(z)$

$C(z) = a + bz$

0   z ∞

We assumed this to be the case in oxidation:

O_2 diffusion through SiO_2 , where

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

For other solutions, consider classical experiment:

Diffusion couple: thin dopant layer on rod face,

press 2 identical pieces together, heat.

Then study diffusion profile in sections.

symmetry

$$\frac{dC(0,t)}{dz} = 0$$

$$C(z,0) = 0 \quad (z \neq 0)$$

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

$$\int_{-\infty}^{\infty} C(z,t)dz = Q = \text{const. (# /area)}$$

$t = 0$

0   z ∞
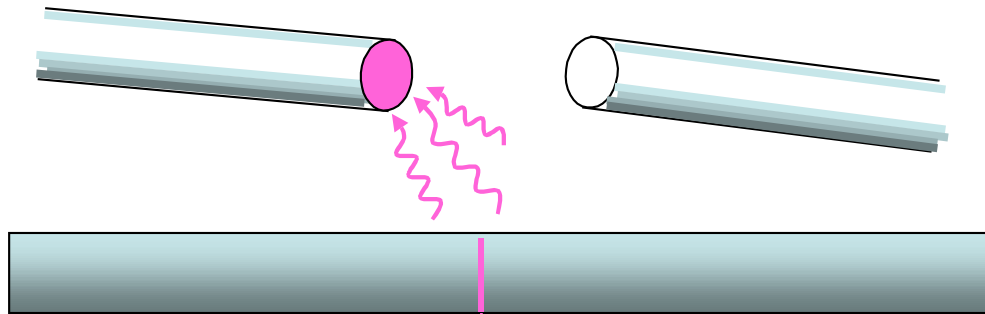
Analytic Solution to Diffusion Equations

$$J = -D\frac{\partial C}{\partial z}, \qquad \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2}$$

I. "Drive in" of *small*, fixed amount of dopant, solution is Gaussian
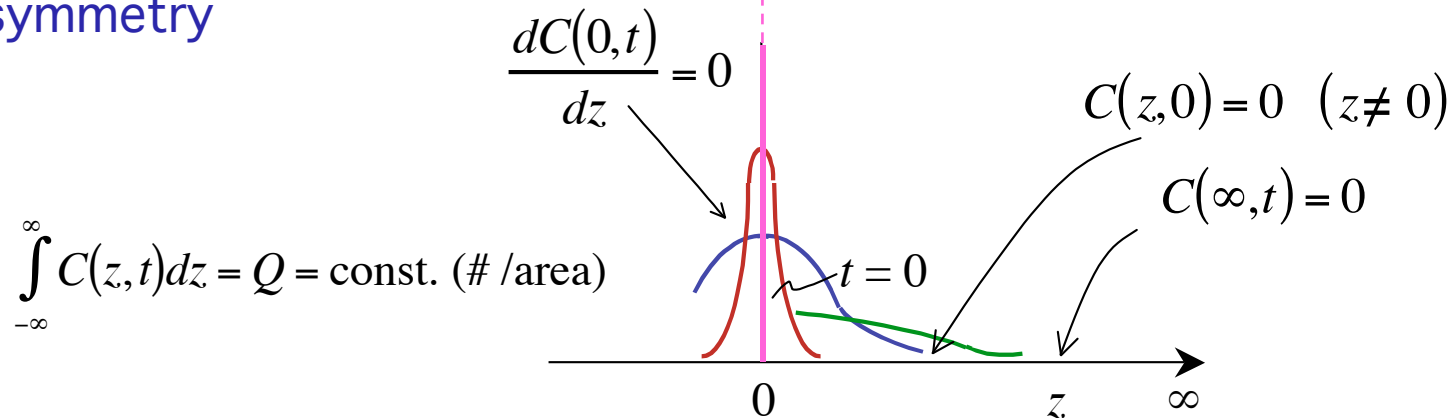
$$\frac{dC(0,t)}{dz} = 0$$

$$C(z,0) = 0 \quad (z \; 0)$$

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

Predeposition is delta function, δ(z).

$$t = 0$$

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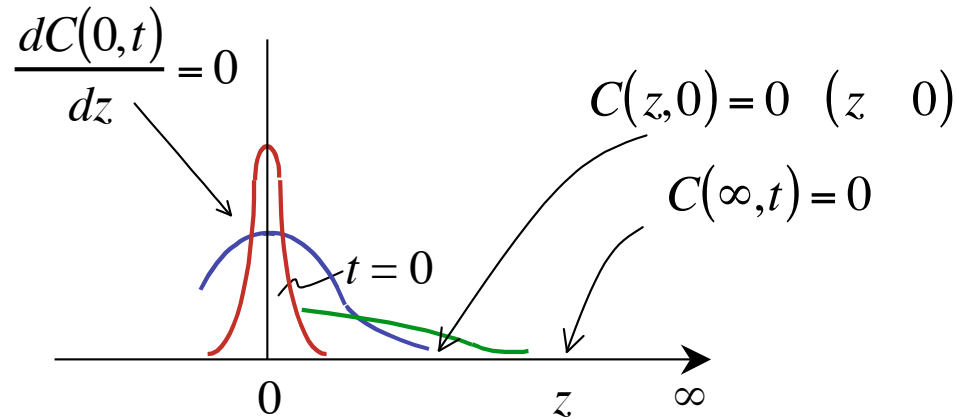
$$C(z,t) = \frac{Q}{\sqrt{\pi D t}}\exp\left[-\frac{z^2}{4Dt}\right] \qquad t > 0 \qquad\qquad \text{Units}$$

$$\frac{1}{2}\text{ Width of Gaussian} = \quad a = 2\sqrt{Dt} \;=\text{diffusion length } a$$

(*a* is large relative to width of predeposition)

Dose, *Q*, amount of dopant in sample, is constant.

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

II. Predeposition

(*Limitless* source of dopant)

$$C(0,t) = C_0$$

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

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

Const C_0
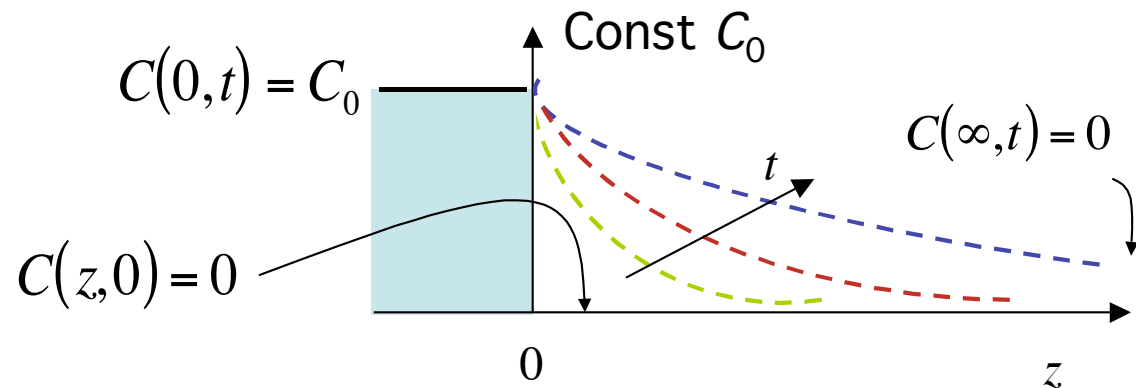
$$C_{imp}(z,t) = \frac{2}{\sqrt{\pi}} \int_0^{u=\frac{z}{2\sqrt{Dt}}} \exp[-\xi^2]\,d\xi \equiv \mathrm{erf}(u) = \mathrm{erf}\left(\frac{z}{2\sqrt{Dt}}\right)$$

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

$t = 0$

C

erf
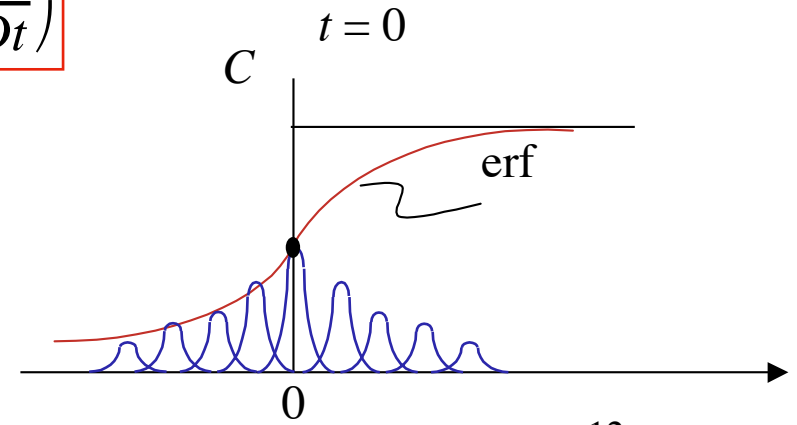
Other I.C./B.C. (cont.):
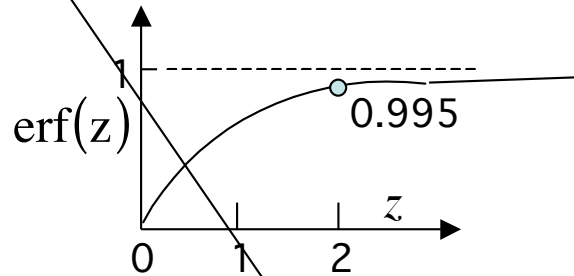
$$\text{erf}C(u) = 1 - \text{erf}(u)$$
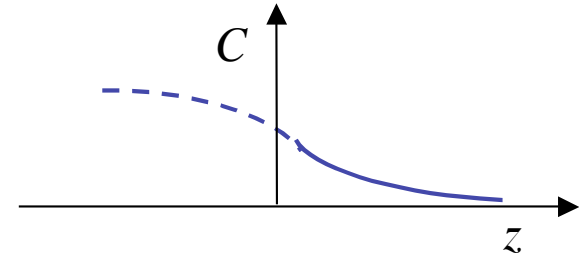
$$C(z,t) = C_{\text{surf}} \text{erfc}\left[\frac{z}{2\sqrt{Dt}}\right], \qquad t > 0$$

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

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

$C(0,t) = C_0$

Const C_0

$C(\infty, t)$

$C(z,0) = 0$
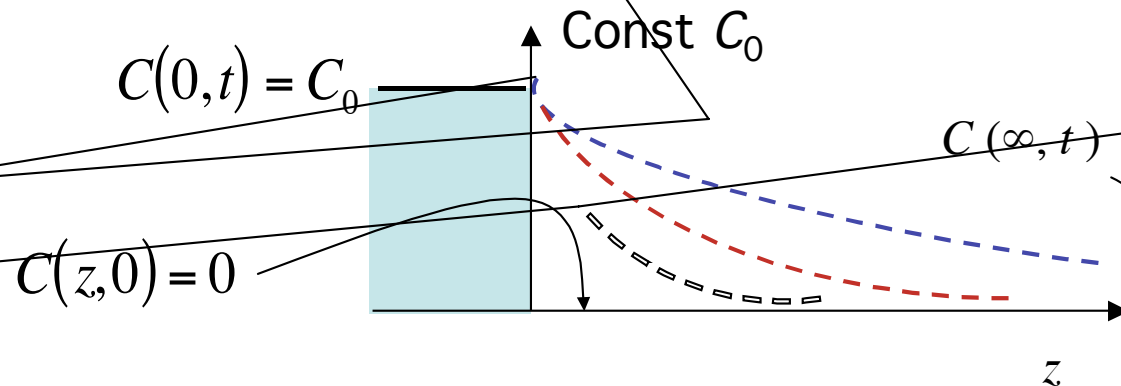
Internal *E* fields alter Fick's Law

Heavily doped layer can generate its own field

due to displacement of mobile carriers from ionized dopants:

P-type Si

C_A

z

C

C_A

Mobile hole concentration

Net charge

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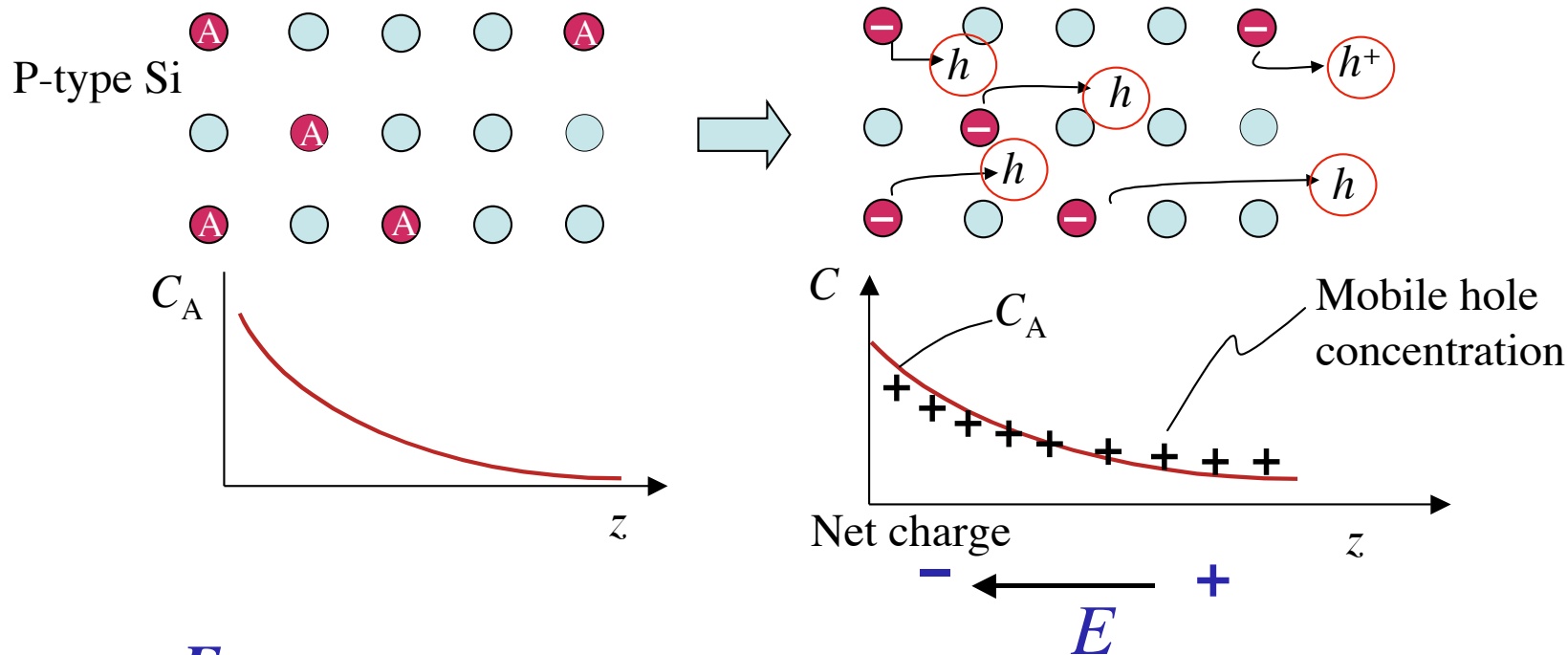
E enhances diffusion of A⁻ to right, (also down concentration gradient).

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

diffusion   **A⁻ *drift***

$$\mu = \frac{Dq}{kT}$$

Einstein relation from Brownian motion

Neutral and charged impurities, dopants

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

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

So vacancies can be charged

Si
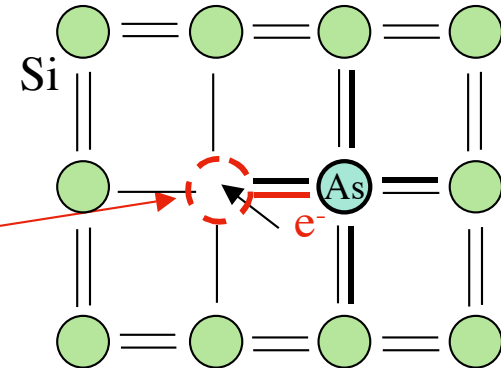
For small dopant concentration, different diffusion processes are independent:

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

electrons   **holes**

(these D^0 are NOT same as single activation energy values)

Intrinsic Diffusivities and Activation Energies of Substitutional Diffusers in Silicon[a]

		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	4.20	3.92
D_i^-	D_0	4.44	22.9	13	—	—	—
	E_0	4.0	4.1	4.0	—	—	—
D_i^2	D_0	44.2	—	—	—	—	—
	E_0	4.37	—	—	—	—	—

[a] D_0 in cm²/s; E_0 in eV.

[Higher activation energy for charged vacancy diffusion]

6.155/ 3.15:   16

"What is n?"

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

n is free electron concentration.   **For strong donor doping $n > n_i$**

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

For intrinsic semiconductor or $N_D < n_i$, $n = p = n_i$

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

See example p. 412 Plummer

$$n_i = 7.14 \times 10^{18}$$

$$D^{\text{eff}}_{\text{As}} = D^0 \qquad + \qquad D^-(n/n_i) \qquad +$$
$$\underbrace{2.67 \times 10^{-16} + 1.17 \times 10^{-15}(n/n_i)}$$

$N_D = 10^{18}$: $D^{\text{eff}}_{\text{As}} = 1.43 \times 10^{-15}$
$N_D = 10^{20}$: $D^{\text{eff}}_{\text{As}} = 16.6 \times 10^{-15}$

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

Exercise

Calculate diffusivity of P in Si at 1000° C for

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

c) compare diffusion length b) with uncharged estimate

---

a) $C_P < n_i = 10^{19}$

from F 1.16

Exercise

Calculate diffusivity of P in Si at 1000° C for

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

    c) compare diffusion length b) with uncharged estimate
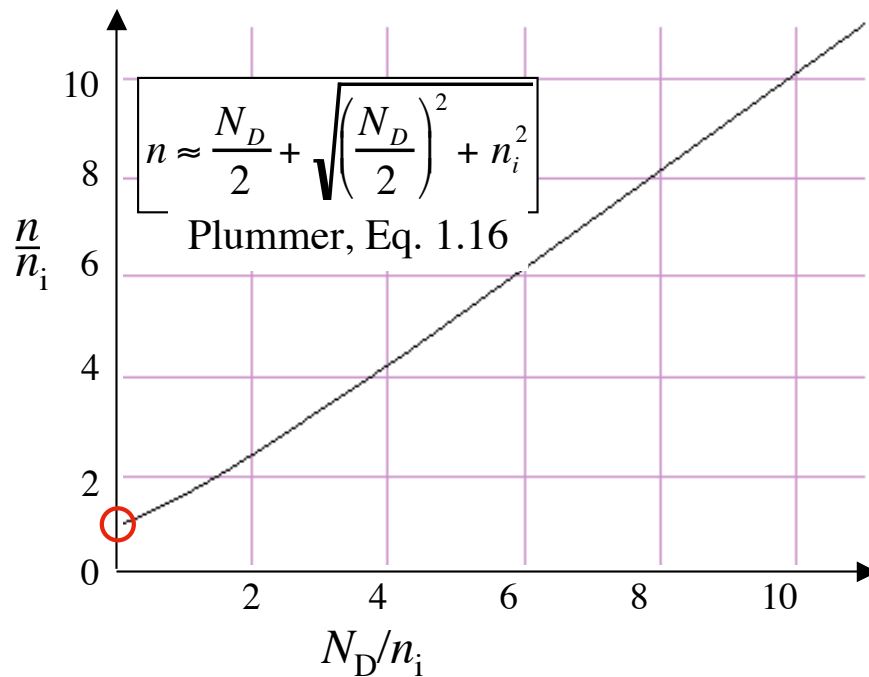
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a) $C_P < n_i = 10^{19}$

Diffusion of P in Si

D_0	E_a	D_0^-	E_a^-
(cm²/s)	(eV)	(cm²/s)	(eV)
3.85	3.66	4.4	4.0

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

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

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

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

Plummer, Eq. 1.16

Better than single-activation-energy:

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

19

Exercise

Calculate diffusivity of P in Si at 1000° C for

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

c) compare diffusion length b) with uncharged estimate

---

b) $C_P = N_D = 4 \times 10^{19}$ $\boxed{n \approx \dfrac{N_D}{2} + \sqrt{\left(\dfrac{N_D}{2}\right)^2 + n_i^2} = 10^{19} + \sqrt{4 \times 10^{38} + 10^{38}}} = 3.24 \times 10^{19}$ cm^{-3}

Plummer, Eq. 1.16

$$D = D_P^0 + D_P^-\left(\dfrac{n}{n_i}\right) = 1.3 \times 10^{-14} + 6.63 \times 10^{-16}\left(\dfrac{3.24}{1}\right) = 1.5 \times 10^{-14} \; (\text{cm}^2 s^{-1})$$ vs 1.37

c) $a = 2\sqrt{Dt}$,   1 hr $\Rightarrow a_0 = 2\sqrt{1.37 \times 10^{-14} \times 3600} = 0.14 \; \mu m$

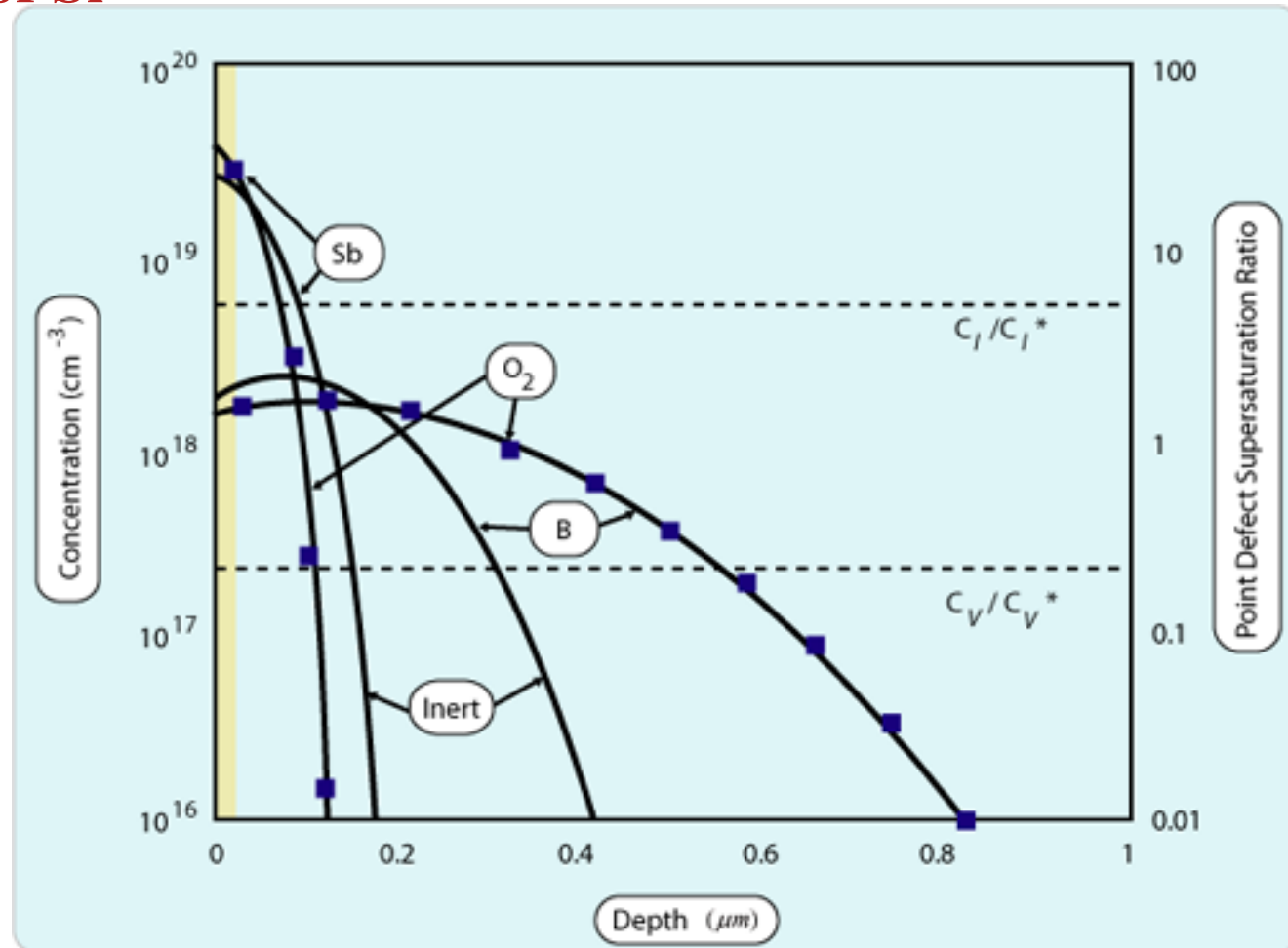$$a_P = 2\sqrt{1.51 \times 10^{-14} \times 3600} = 0.147 \; \mu m$$

Consequence:

Diffusion is enhanced
at high dopant
concentrations
$\Rightarrow$ Sharper
  diffusion profile

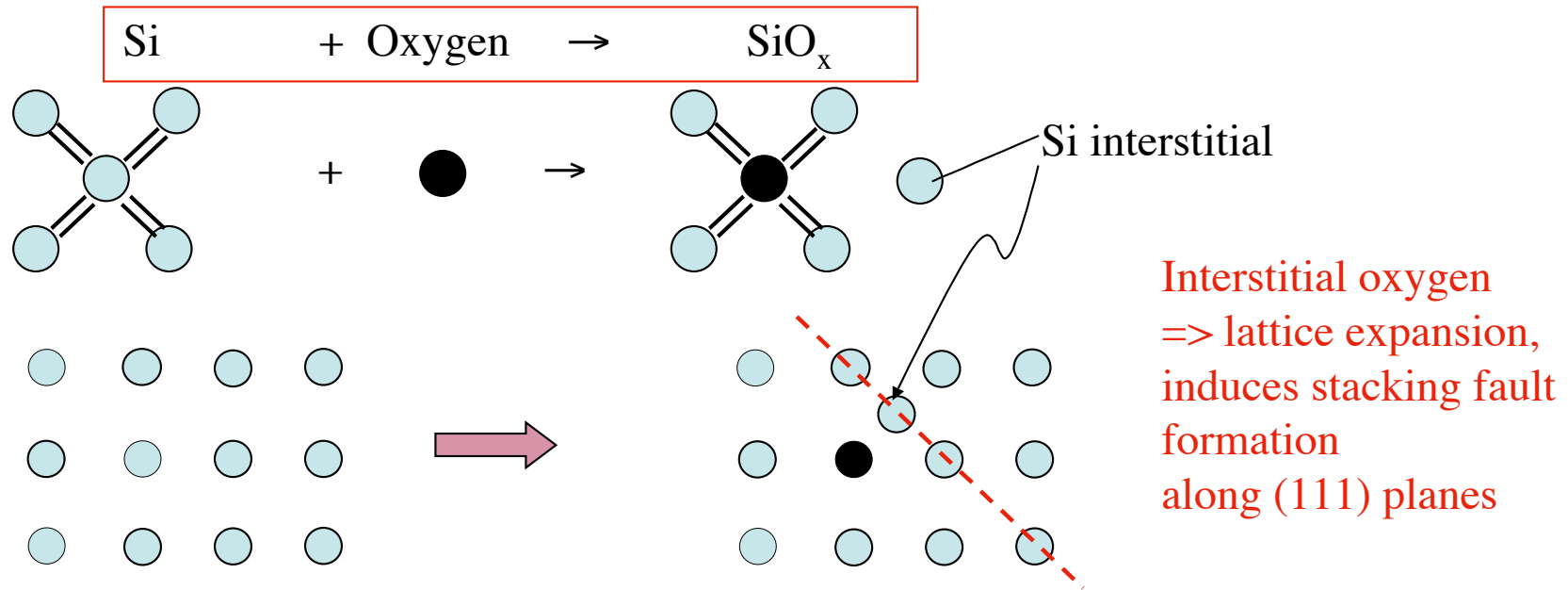# Effect of oxidation of Si
on diffusion

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

So far
we have concentrated on
diffusion
by vacancy mechanism

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

Effect of oxidation on diffusion in Si

$$Si \quad + \quad Oxygen \quad \rightarrow \quad SiO_x$$

Si interstitial

Interstitial oxygen
=> lattice expansion,
induces stacking fault
formation
along (111) planes

Because B and P can diffuse via vacancies as well as interstitial process
their diffusion is enhances by oxidation.

But Sb is large and diffuses only by vacancies.

Si interstitials created by oxidation,

recombine and reduce concentration of vacancies

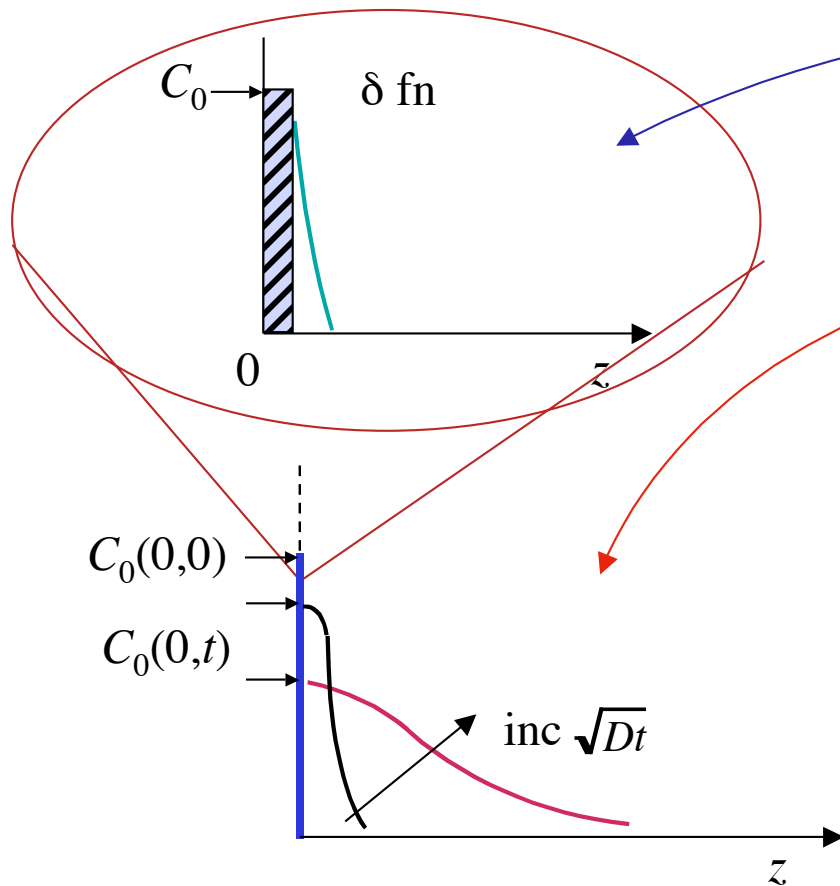suppressing diffusion of Sb atoms.
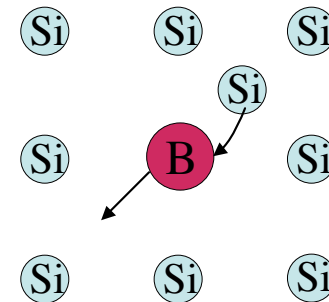
Review: Doping and diffusion, *small dose*

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

Plus I.C. and B.C.s

If "predeposition" is *small* dose,

followed by a higher *T*,

larger *t* (larger $a \sim \sqrt{Dt}$)

"drive-in" process.

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

2) B.C. $C(\infty, t) = 0$
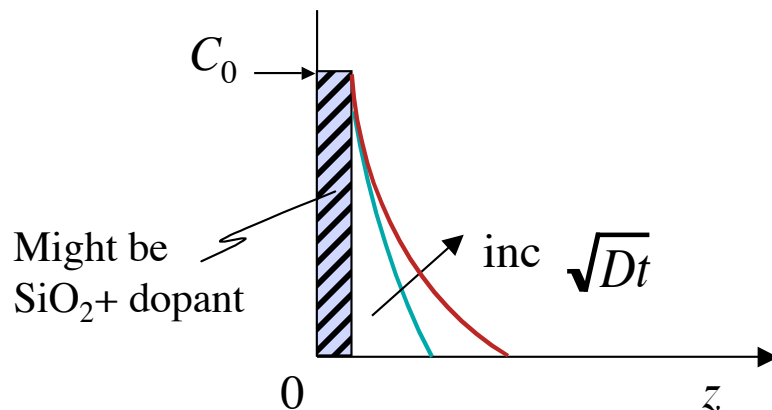
3) <u>Fixed</u> dose $Q = \dfrac{a}{\sqrt{\pi}} c_0$

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

$$C(0,t) = \frac{Q}{\sqrt{\pi Dt}}$$ 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. $C(z, 0) = 0$ $z > 0$

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

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

C_0

Might be
SiO_2+ dopant

inc $\sqrt{Dt}$

0

z

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

$$\text{Dose} \equiv Q = \int_0^\infty C(z,t)dz = \frac{2\sqrt{Dt}}{\sqrt{\pi}}C_0 = \frac{a}{\sqrt{\pi}}C_0$$
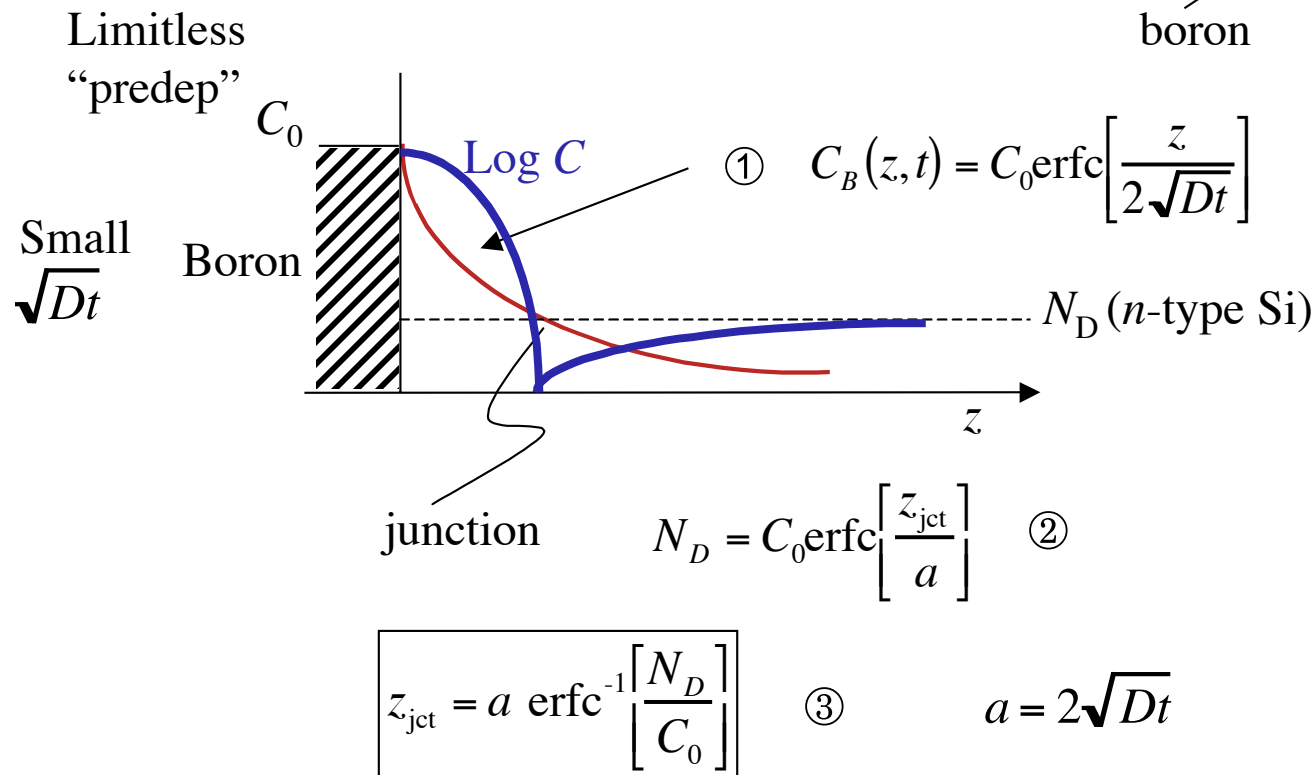
C_0 limited by solid solubility
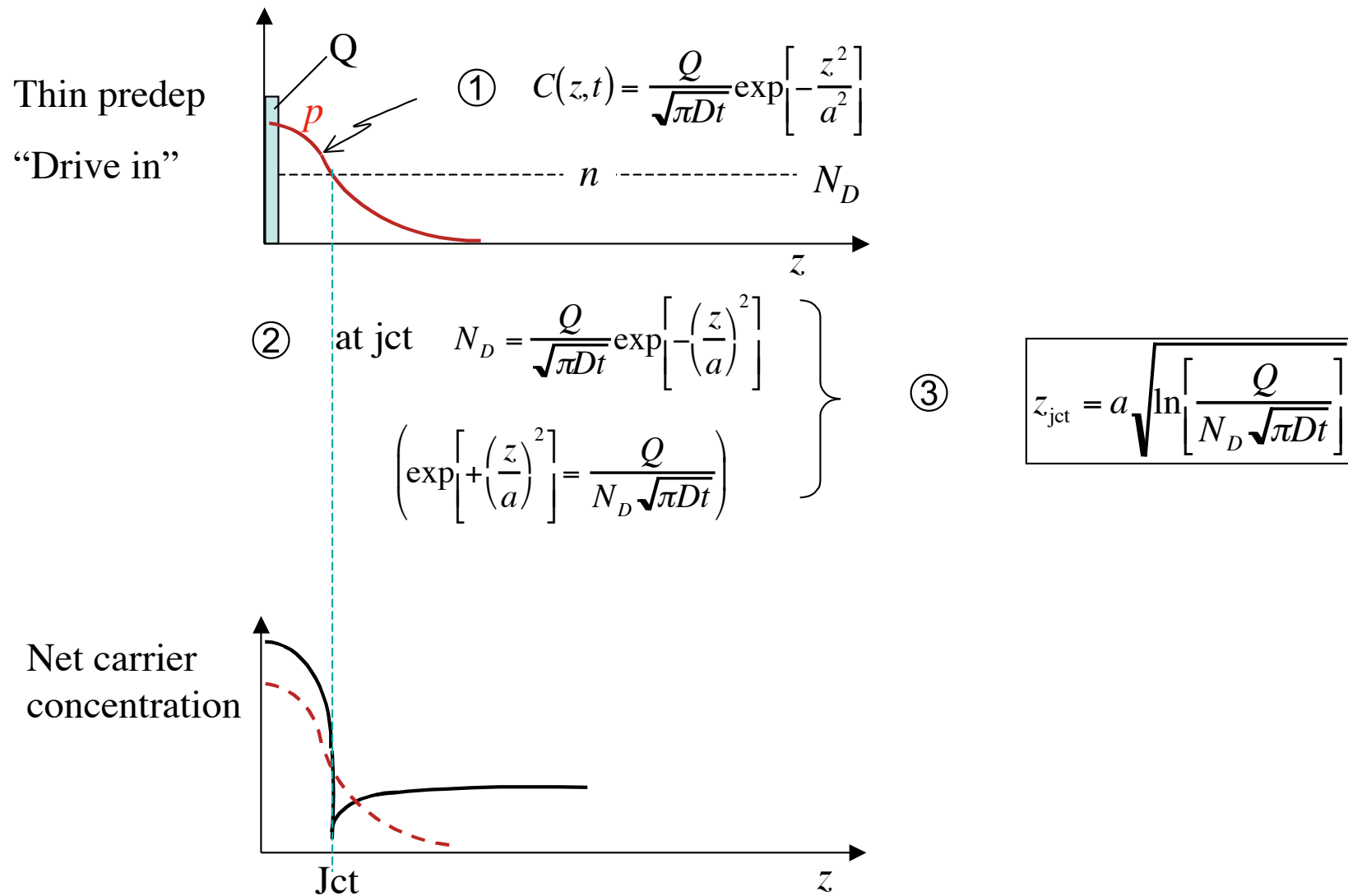
Junctions between different doped regions

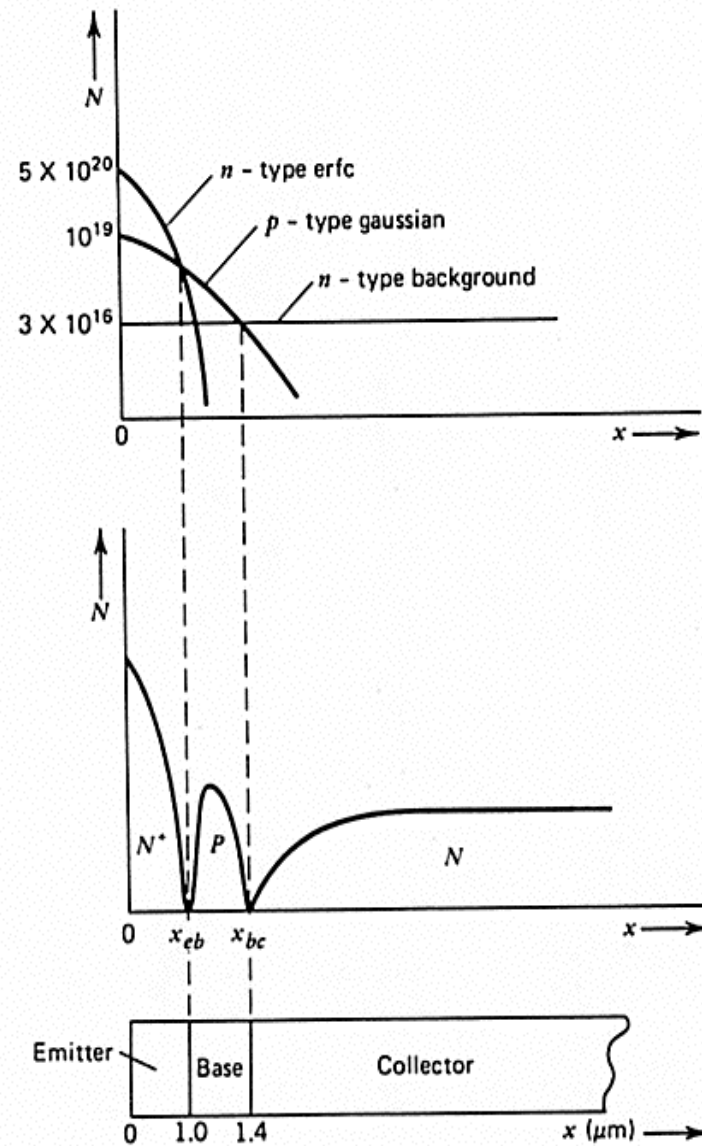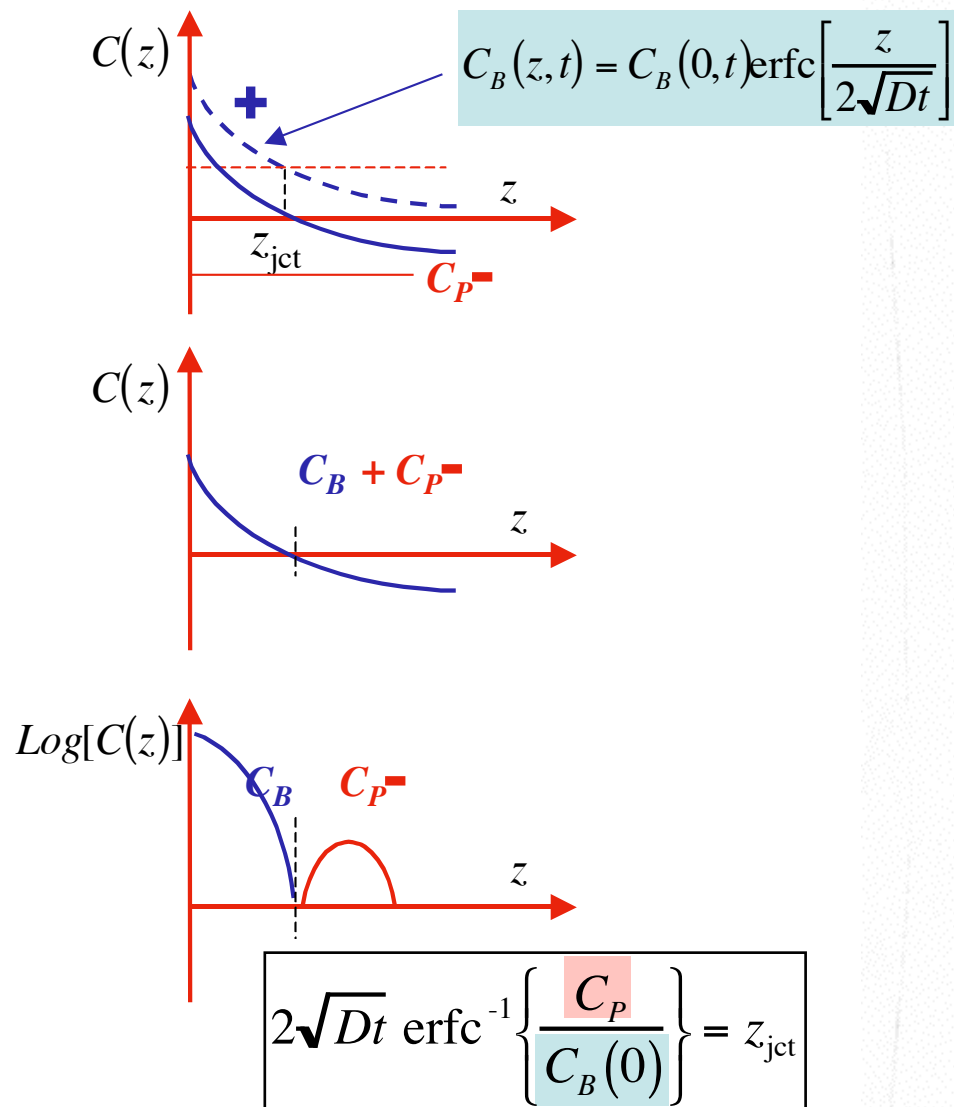Diffuse B at high concentration, into n-type Si, (uniformly doped, N_D, with P).
Want to know depth of p.n. junction ($N_A = N_D$)

boron   phosphorus

Limitless
"predep" C_0

Small
$\sqrt{Dt}$ Boron

Log C ① $C_B(z,t) = C_0 \mathrm{erfc}\left[\dfrac{z}{2\sqrt{Dt}}\right]$

N_D (n-type Si)

z

junction $N_D = C_0 \mathrm{erfc}\left[\dfrac{z_{jct}}{a}\right]$ ②

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

Junctions between different doped regions

Thin predep

"Drive in"

$$① \quad C(z,t) = \frac{Q}{\sqrt{\pi Dt}} \exp\left[-\frac{z^2}{a^2}\right]$$

Q

p

n — — — N_D

z

$$② \quad \text{at jct} \quad N_D = \frac{Q}{\sqrt{\pi Dt}} \exp\left[-\left(\frac{z}{a}\right)^2\right]$$

$$\left(\exp\left[+\left(\frac{z}{a}\right)^2\right] = \frac{Q}{N_D \sqrt{\pi Dt}} \right)$$

③

$$z_{jct} = a \sqrt{\ln\left[\frac{Q}{N_D \sqrt{\pi Dt}}\right]}$$

Net carrier
concentration

Jct

z

$$C_B(z,t) = C_B(0,t)\,\text{erfc}\left[\frac{z}{2\sqrt{Dt}}\right]$$

$$2\sqrt{Dt}\ \text{erfc}^{-1}\left\{\frac{C_P}{C_B(0)}\right\} = z_{\text{jct}}$$

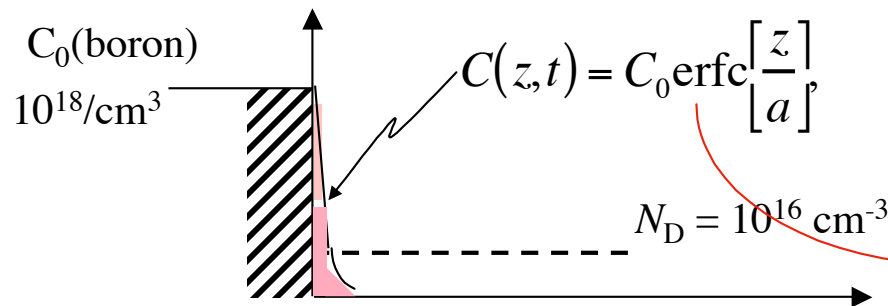# Exercise

N-type Si, $N_D = 10^{16}$ cm^{-3} is doped with boron by a "predep"

from a const source with C_0 (boron) = 10^{18} cm^{-3}

C_0(boron)
10^{18}/cm^3

$$C(z,t) = C_0 \mathrm{erfc}\left[\frac{z}{a}\right],$$

$N_D = 10^{16}$ cm^{-3}

Question:

If predep is done at 1000°C for 1 hr,

what is junction depth?

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

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

From appendix, $x = 1.82$

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

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

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

6.155/ 3.155J 9/29/03

30

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

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

z_{jct}

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

1 hr t
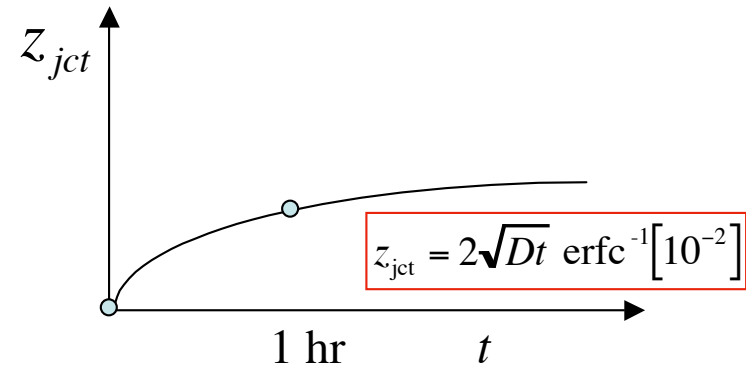
Question: Now surface film (const. source) is removed

and this dose, $C(z, 1hr)$, is " driven in" for 1 hr at 1100°C.

Now where is junction?

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

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

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

Measuring diffusion profiles

Resistance

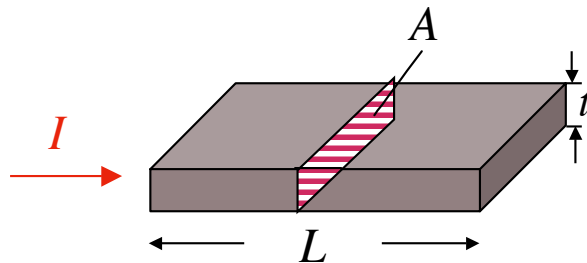$$R = \rho \frac{L}{A} \, (\Omega),$$

resistivity

$$\rho = \frac{RA}{L} \, (\Omega m)$$

conductivity

$$\sigma = \frac{1}{\rho} = nq\mu$$

But n, μ are functions of position due to doping

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

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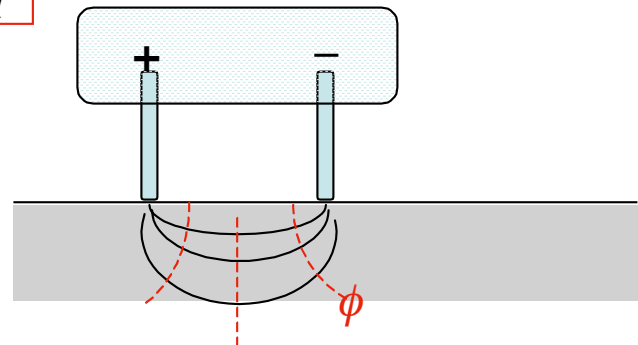
Define

sheet resistance

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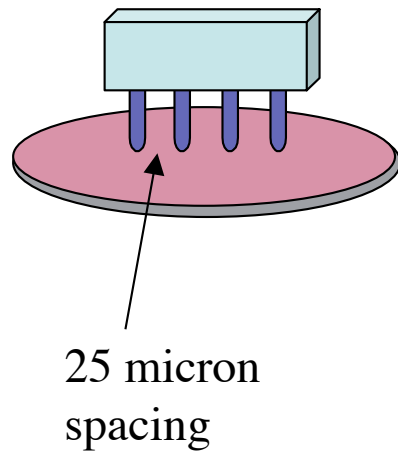
an average measurement of n

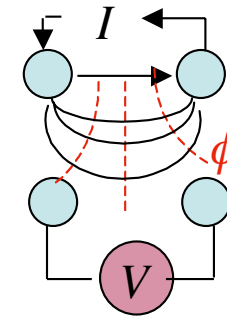Spreading resistance probe:
(Developed at Bell Labs in '40s)

ϕ

Measuring diffusion profiles

4-point probe
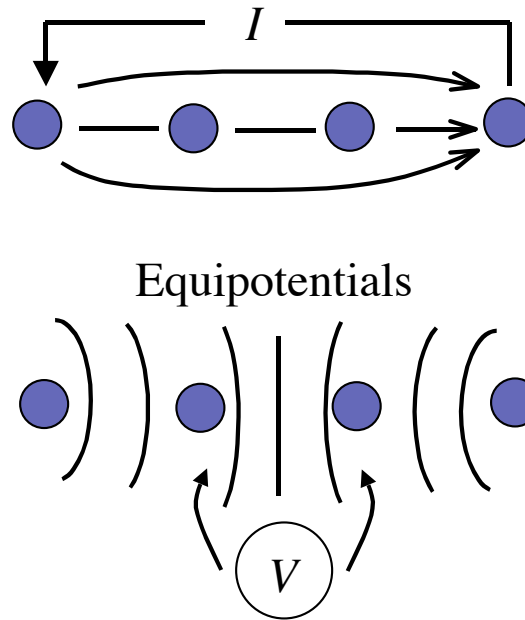
Also square array

(Van der Pauw method)

I

Equipotentials

V

φ

I

V

25 micron
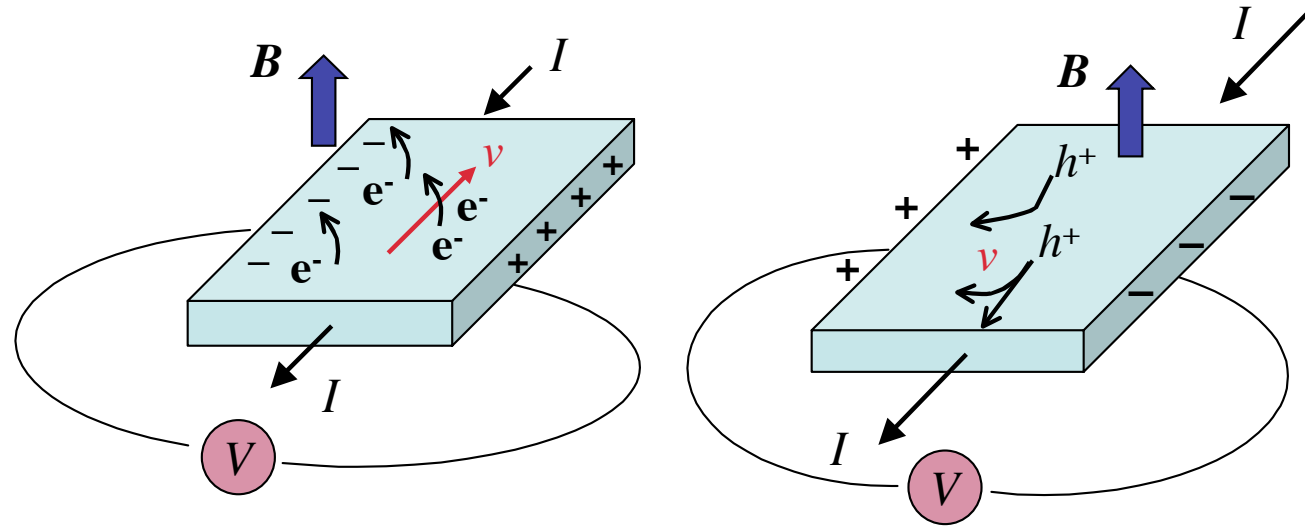spacing

These $\Rightarrow$ average *n* if done from surface.

These are most useful if done on beveled wafer:

Polish off $\Rightarrow$ depth profile

sample
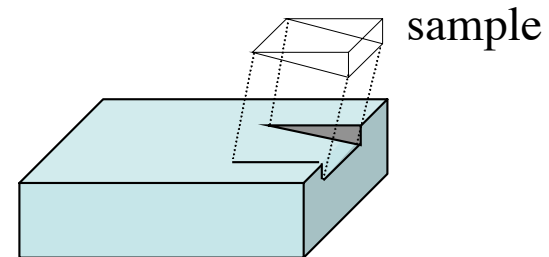
Hall effect: electrical transport in magnetic field.

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

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

$$\frac{F}{q} = E_H = \frac{J}{nq} B$$

$$\boxed{E_H = R_H(J \times B)}$$

Hall coefficient => charge sign and concentration

R_H is slope of V vs B data

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

Large hole Concentration p

Small electron concentration n
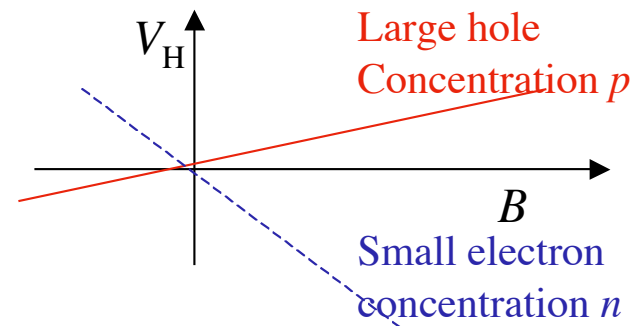
Again an average measurement

Capacitance

Use MOS structure, gate & substrate are electrodes

Useful for lightly doped regions

$$C = \frac{\varepsilon A}{d}$$
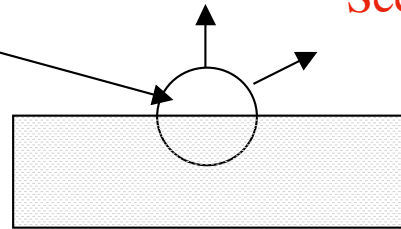
Depletion width

SIMS

(Secondary ion mass spectroscopy)

Ion source

1 - 5 k eV
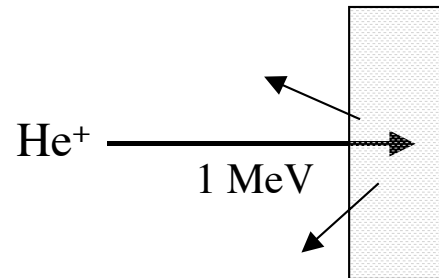
Sputters surface

Secondary ions

to mass spectrometer

Depth profile

RBS

(Rutherford back scattering)

He$^+$

1 MeV

Ions penetrate

Backscatter energy

depends on depth and impurities

Backscatter intensity $\propto$ (mass impurities)^2