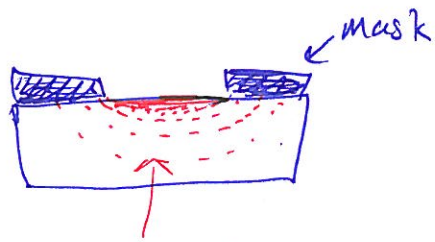
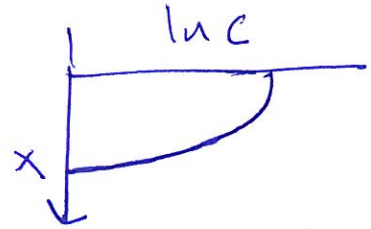
7. Impurity Doping and ~~implantation~~

— controlled amounts of impurities to control electrical properties

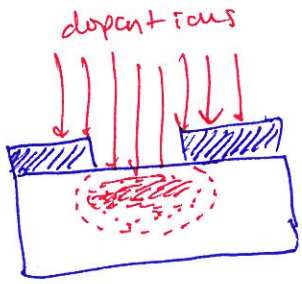
A. Diffusion →

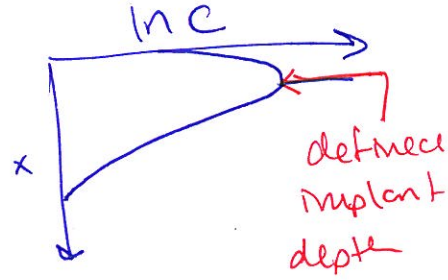




impurities drive in via diffusion

B ion-implantation





Both processes used as they complement each other.

Sze 13.1

Basic Diffusion Process

P, As – common n-type

B – common p-type

Solid Sources

BN, As_2O_3, P_2O_5

(dopant wafers or spin-on dopants)

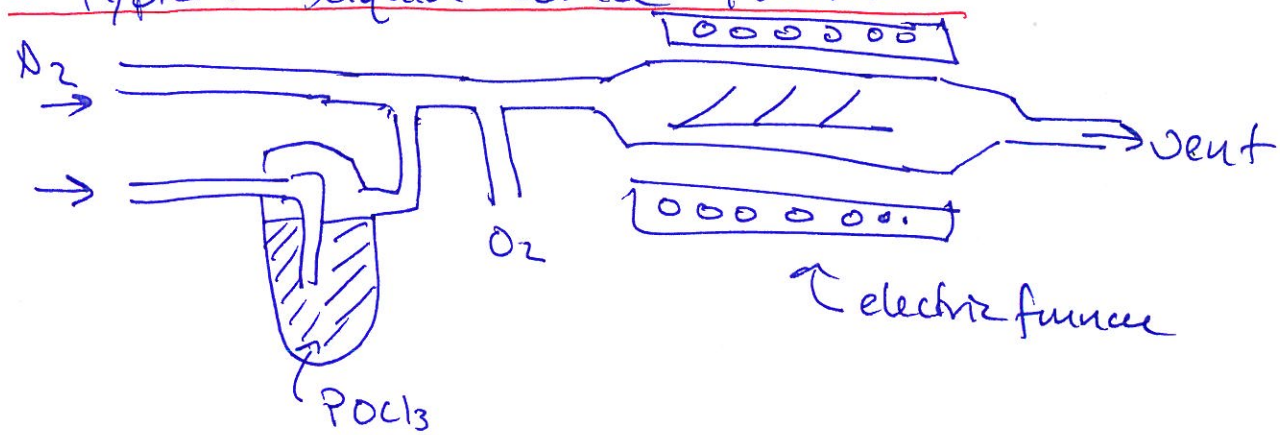
Liquid Sources

BBr_3, $AsCl_3$, $POCl_3$

Gas Sources

B_2H_6, AsH_3, PH_3

* Typical liquid-Source doping Furnace



$$4\,POCl_3 + 3O_2 \longrightarrow 2\,P_2O_5 + 6\,Cl_2$$

$$2P_2O_5 + 5Si \longrightarrow 4P + 5SiO_2$$

* Si reduces the P_2O_5 to P, and Entropy drives the diffusion of the P into the Si wafer.

* (process w/ GaAs involves methods to prevent As evaporation at the high temperatures)

GaAs*

→ As overpressure w/ $ZnAs_2$

→ ZnO/SiO_2 cap

etc.

7.3 The Diffusion Equation

a. → motion via interstitials or vaccancies

b. → Basic process similar to diffusion of electrons and holes

define flux = $\boxed{F = \#\text{ dopant atoms} / \text{time} \cdot \text{area}}$

$\boxed{C = \#\text{ dopant atoms} / \text{Volume}}$

$$\boxed{F = -D \frac{\partial C}{\partial x}}$$ Fick's first law of diffusion

concentration gradient driving force for diffusion

From continuity equation (with no "generation"/"recombination" of impurities)

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

time change of concentration in small element must be related to change in flux over distance...

for D independent of C (valid for low concentrations of impurities in the sample)

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

Just Fick's Second Law

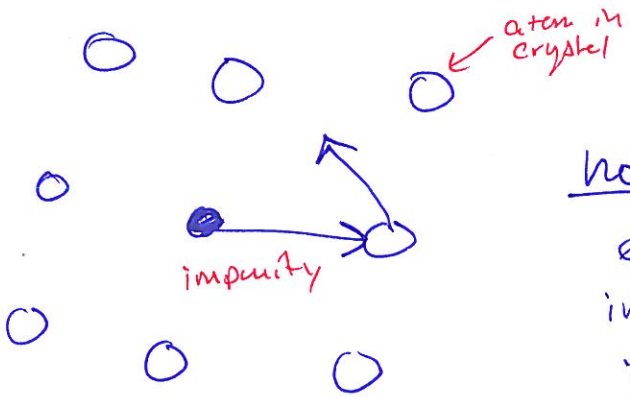
Furthermore, Experiment shows that diffusion is temperature activated:

$$D = D_0 \exp\left(-E_a / kT\right)$$

activation energy

D_0 extrapolated to infinite T

~ $\boxed{E_a > 3\,eV \rightarrow \text{vacancy mechanism}}$



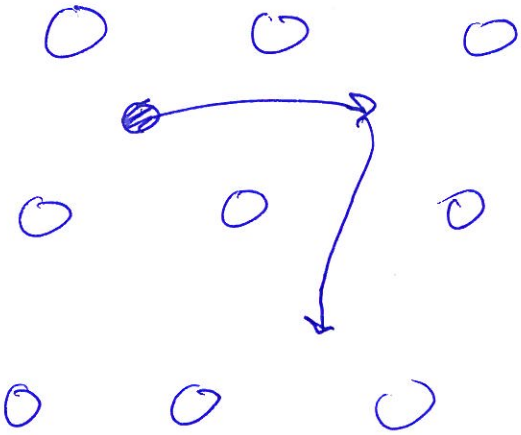
host atom thermally excited to ~~impurity~~ interstitial position. impurity fills vacancy.

O, C, Al, Ga, B, ...
$D_s \sim 10^{-8} - 10^{-14}\ cm^2/s$

(eg. As in Si is slow, vacancy diffusion.)

~ $E_a < 2eV \rightarrow$ interstitial mechanism

(eg. Cu in Si)



- Interstitial Diffusion
- lower barrier height.

D's range from $10^{-3} - 10^{-6}\ cm^2/s$ ...

Cu, Li, H, Au, Na

in Si

Diffusion Profiles

— depend on initial and boundary conditions

Two important cases:

A. Constant Surface Concentration
B. Constant ~~total~~ dopant diffusion

A. Constant Surface Concentration

$$\boxed{C(x,0) = 0}$$ initial condition

Boundary Conditions: $C(0,t) = C_s$ ← at $x=0$ you have surface concentration which is constant

$C(\infty, t) = 0$ ← far away from interface there is nothing

→ find equation $\boxed{C(x,t)}$ that satisfies

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

a Solution is:

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

Diffusion length

D units cm^2/s
t units s

$\sqrt{Dt} = \underline{\underline{cm}}$

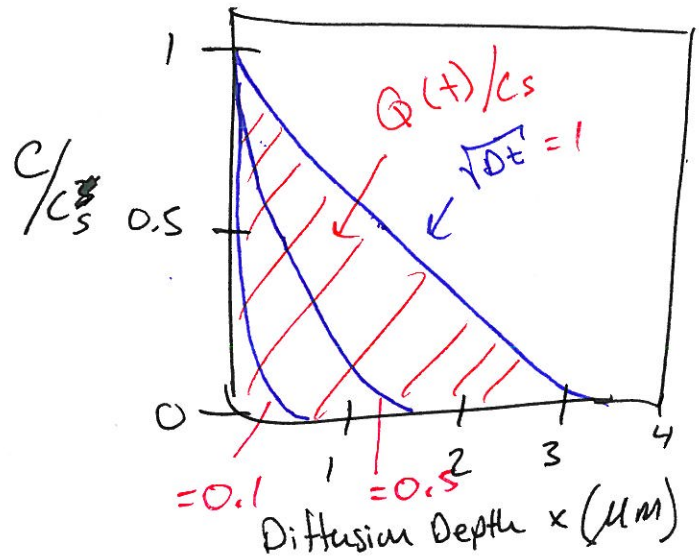
... average diffusion distance for given time.

Note

erfc is the complementary error function

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

$$\mathrm{erfc}(x) = 1 - \mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt$$



Substitute in error function equation

$$Q(t) = \int_0^\infty C(x,t)\,dx$$

$$\boxed{Q(t) = \frac{2}{\sqrt{\pi}} C_s \sqrt{Dt}}$$

$$\cong 1.13 C_s \sqrt{Dt}$$

$\boxed{Q(t) \text{ is area of diffusion profile (near to triangle)}}$

~~Show~~ by differentiating we get $\boxed{\left.\frac{\partial C}{\partial x}\right|_{x,t} = \frac{-C_s}{\sqrt{\pi D t}} e^{-x^2/4Dt}}$

→ which could be important if there is a large gradient in the device zone.

Constant-Total-Dopant Diffusion

→ fixed amount of dopant is deposited onto the semiconductor in thin layer → subsequent "drive in"

Boundary Conditions:

$$\int_0^\infty C(x,t)\,dx = \underline{S}$$ → total amount of dopant per unit area.

and $C(\infty, t) = 0$ → semi-infinite boundary conditions

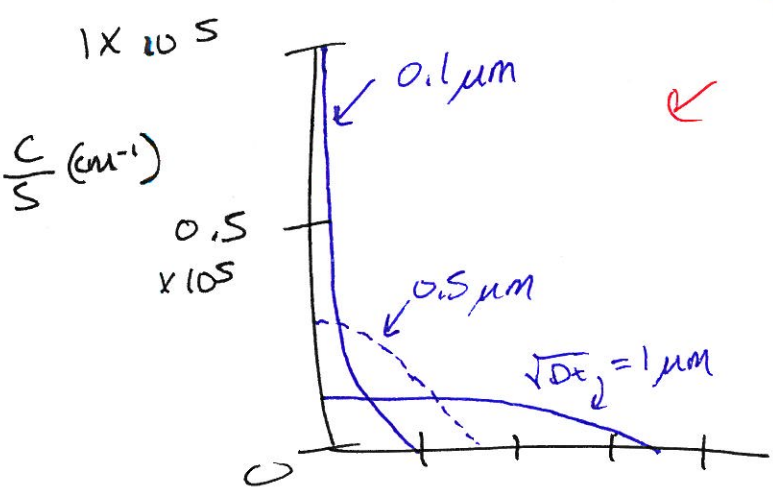
Solution of the diffusion equation:

$$C(x,t) = \frac{S}{\sqrt{\pi D t}} \exp\left[-\frac{x^2}{4Dt}\right]$$

→ gaussian function

$$C(0,t) = C_s(t) = \frac{S}{\sqrt{\pi D t}}$$ <u>surface concentration</u>

→ Surface concentration decreases



Relevant to I.C. processing

"predeposition" → constant surface layer formed
(small $\sqrt{Dt}$)

"Drive-in" (or dopant redistribution step)
diffusion
(~~for~~ much larger $\sqrt{Dt}$)

→ pre-deposition ~ delta function

Evaluation of diffused Layers

① sheet resistance via 4-probe technique

$$R_s = \frac{1}{q\int_0^{x_j} \mu C(x)\,dx}$$

junction depth assume lightly doped water
x where p=n.

Sheet resistance

$R_s = \rho/t$

mobility (average as carriers simple space)

distribution function

- for given profile average resistivity $\boxed{\bar{\rho}} = R_s x_j$

average resistivity of all the Si that has been doped one carrier type.

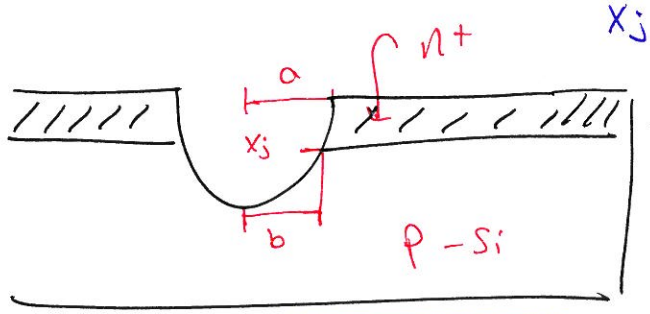
$R_s = \bar{\rho}/x_j \rightarrow \boxed{\bar{\rho} = x_j R_s}$
(by definition)

→ given substrate doping concentration and C_s → unique solution given $\bar{\rho}$!

② Etching method → groove + "Stain" (crude)

$x_j \cong \frac{a^2-b^2}{2R_0}$ → $R_0 \gg a, b$

draw shallow groove →



I measure x_j directly at edge

→ contrast via etching in 100 cm³ HF + dilute HNO_3

→ what causes contrast? must be difference in etching rate and resulting nanostructure

③ Capacitance-Voltage Profiling

* (as you learned in Device Physics Course) *

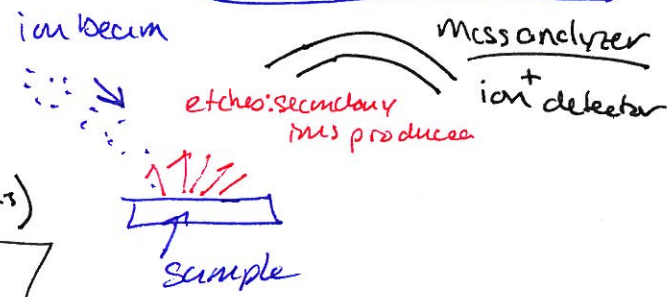
④ SIMS → secondary ion mass-spectrometry

→ most commonly used!

highly sensitive ($< 10^{14}$ cm^{-3})

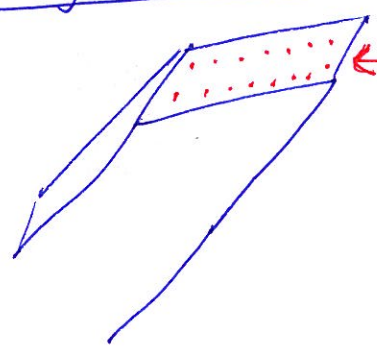
→ $10^{12} - 10^{16}$ /cm³

→ mass selective



⑤ also for Si and Ge,

folks often measure the spreading resistance profile



find R as f(bevel)
use data to reconstruct doping profile
(Solecon Labs)

Extrinsic Diffusion

→ previous derivation assume $\underline{D}$ is constant

→ true when doping less than $\boxed{n_i(T)}$

for doping temperature

$$n_i = p_i = \sqrt{N_v N_c}\, \exp\left[\frac{-E_g(T)}{2kT}\right] \quad cm^{-3}$$

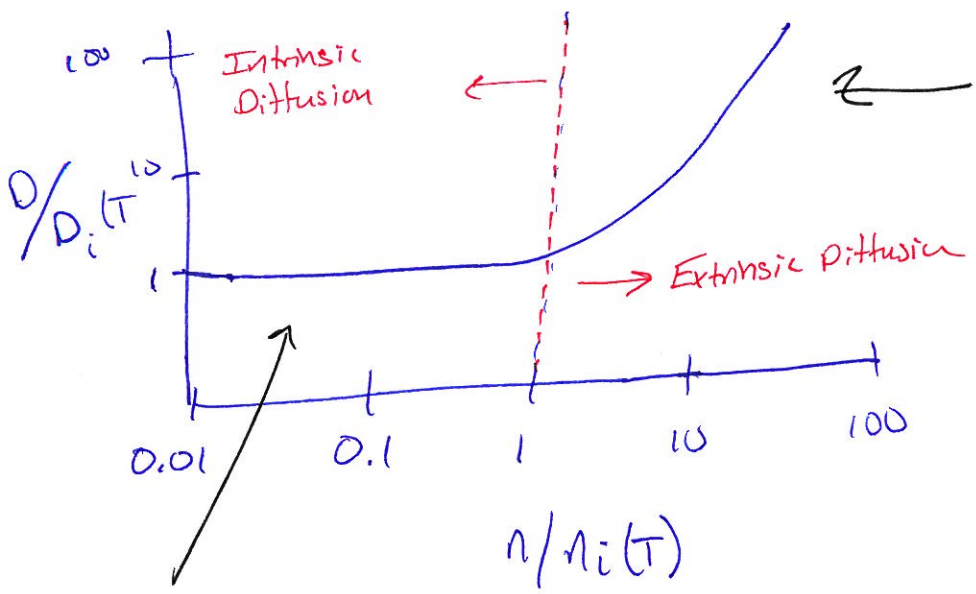
Eg @ $T = 1000°C$, $n_i = 5 \times 10^{18}$ (Si)

and 5×10^{17} (GaAs)

$C(x) < n_i$ → carriers act independent of each other

---

if $C(x) > n_i$, D is a function of concentration



← carriers you add >> than carriers already there. (E_f moves!)

carriers you add don't "matter" relative to carriers already there

Concentration - Dependent Diffusivity

Impurities Dominate Diffusion of species in Si. (see Wolf 9.3 for full explanation)

(– mediated mech.)

① Host Atom gets "displaced" from lattice to interstitial spot via lattice vibration.

Ex. Vacancy ⇒

→ makes vacancy

V^0 → neutral vacancy

V^- → acceptor vacancy

V^{2-} → double-charged acceptor vacancy

V^+ → donor vacancy

because vacancies are charged, their formation affected by E_F

another way to say this:

→ a charged vacancy has a lower energy of formation so more form.

Simple Model of Sze:

$$C_V = C_i \exp\left(\frac{E_F - E_i}{kT}\right)$$

C_V: vacancy concentration

C_i: intrinsic vacancy concentration

low doping $C_V = C_i$, $E_F = E_i$

high doping $C_V > C_i$, $E_F > E_i$

→ D is C-dependent ... must use

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

- form of Ficks Second law.

→ very difficult to solve analytically

→ easy to simulate numerically (see WOLF and discussion therein)

Write diffusion coefficient as:

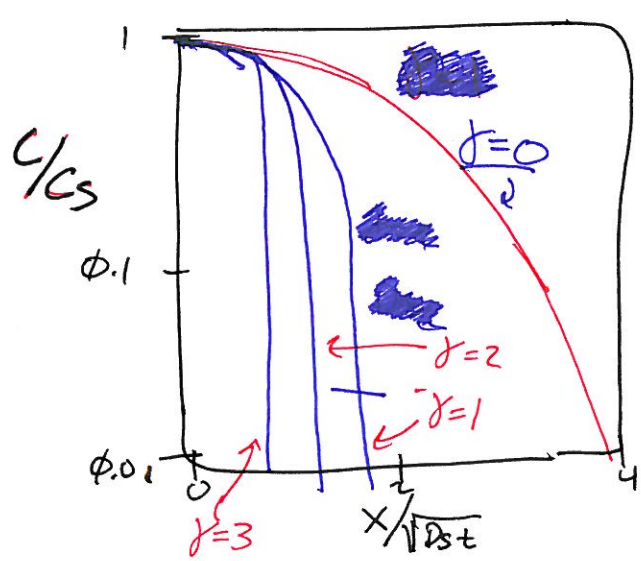
$$\boxed{D = D_s \left[\frac{C}{C_s}\right]^{\gamma}}$$

γ — single parameter to describe doping dependence of diffusion coefficient.

C_s — Surface Concentration

D_s — D at the surface

→ enhanced diffusion leads to sharper diffusion profiles → x_j roughly independent of background concentration (because so sharp)



$X_j = 1.6\sqrt{D_s t}$ $\gamma = 1$

$X_j = 1.1\sqrt{Dt}$ $\gamma = 2$

$= 0.87\sqrt{Dt}$ $\gamma 3$

highly abrupt junction when diffusion into opposite dopant type

SiO_2 as Mask for doping

① Using oxides as masks – Basis of integrated circuit technology

$D_{SiO_2} << D_{Si}$ so SiO_2 effective mask

② At 1000°C dopant reacts w/ SiO_2 to incorporate into the amorphous glass

③ after glass forms, dopant diffuses through glass and enters Si

$$\boxed{D\text{'s in } SiO_2 \sim 10^{-19}\ cm^2/s}$$

$$\boxed{D\text{'s in } Si \sim 10^{-8} - 10^{-14}\ cm^2/s}$$

Thickness of <u>mask</u> needed approx $\boxed{L = \sqrt{Dt}}$

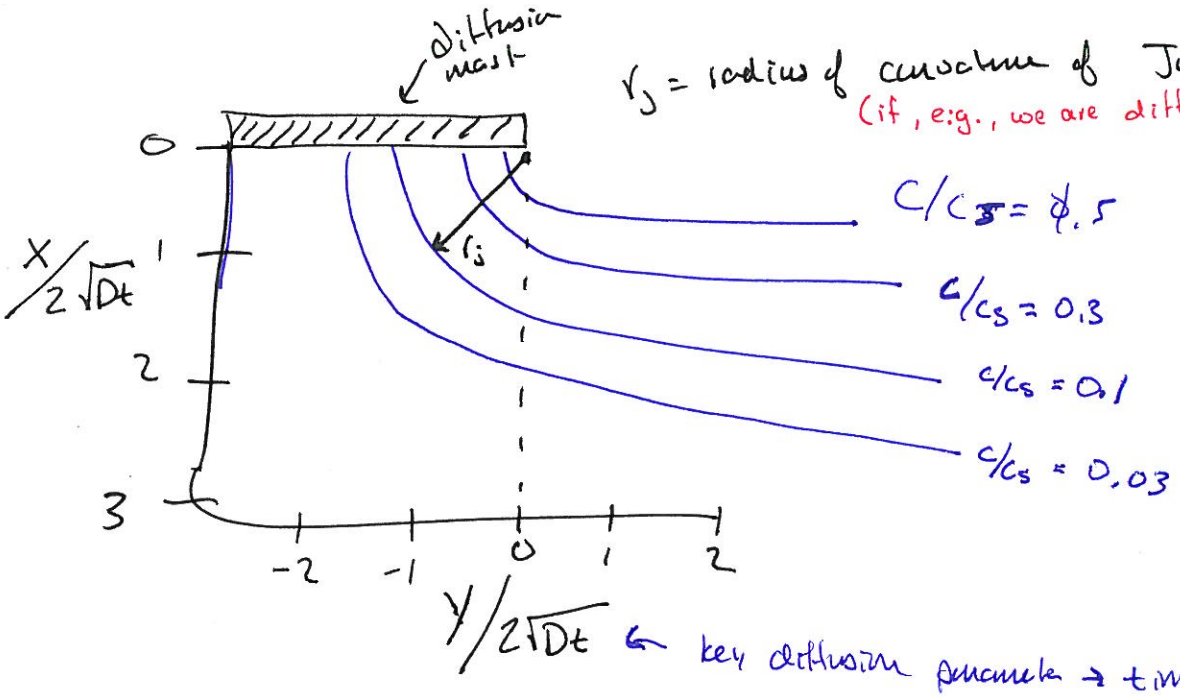
Example: At 1000°C, 100Å of SiO_2 is an effective mask for ~1000 minutes of B diffusion

At 1000°C, need 10,000Å to be effective mask for 1000 minutes for P

Diffusion Related Processes

Lateral Diffusion

- edges (of masks)
- need 2D diffusion equation



← key diffusion parameter → time Diffusion-length product

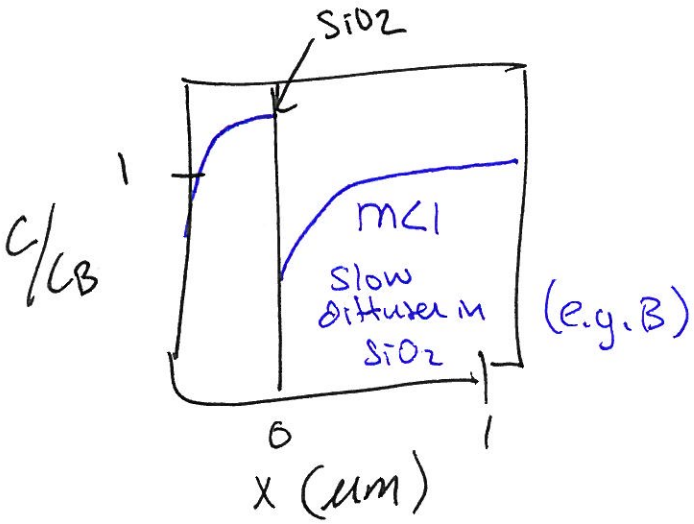
→ junction curvature effect → lower breakdown voltage as field is $\propto r_j$

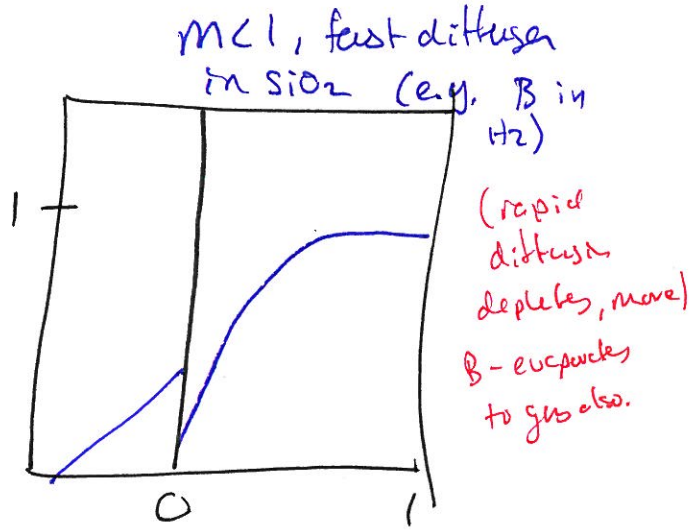
→ lateral penetration is about 3/4 of depth penetration of the dopant.

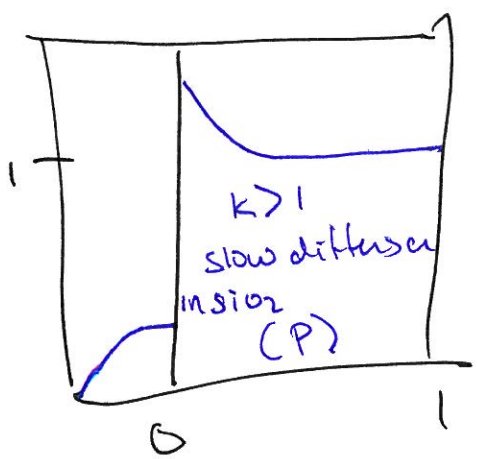
Dopants redistribute during oxidation

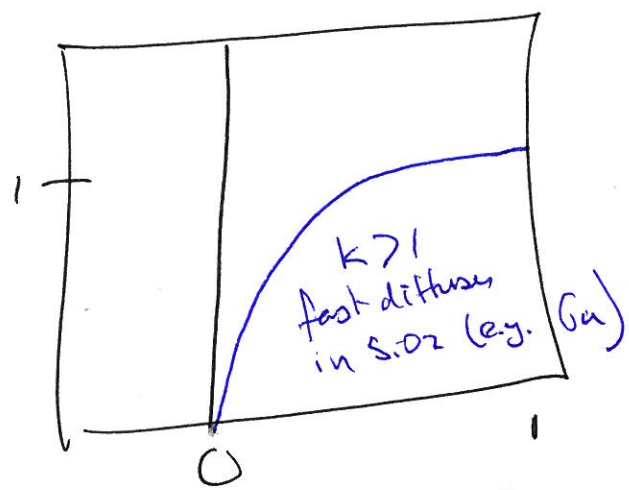
(as discussed previously)

$$m = \frac{C_{dopant,Si}}{C_{dopant,SiO_2}}$$ @ Equillibrium.





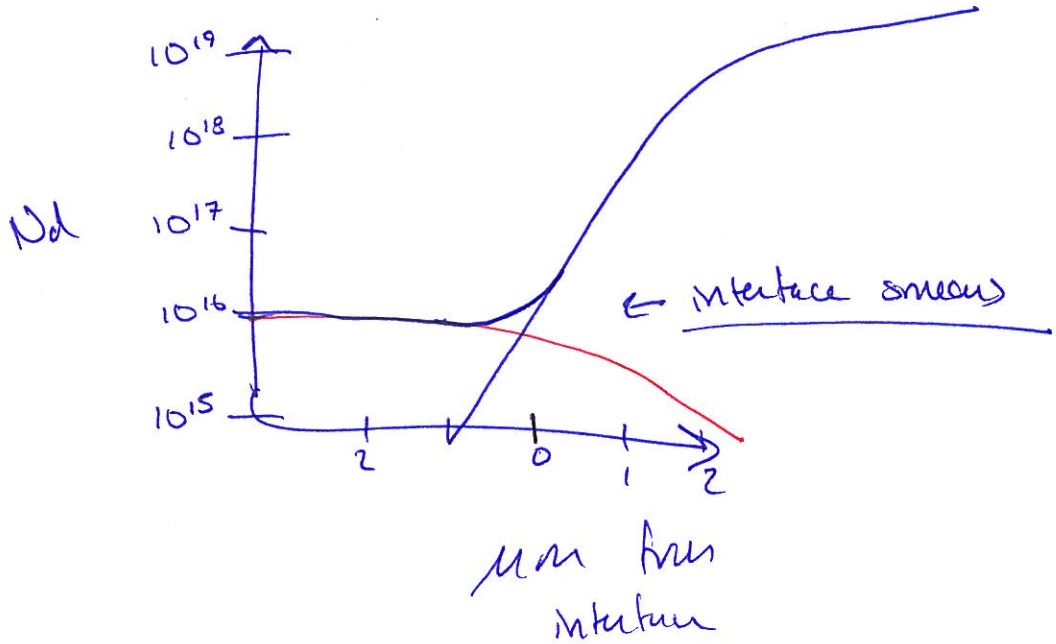




gallium prefers Si → but at diffusion T evaporates!

Same effect occurs during epitaxial growth of Si on Si, ~~[illegible]~~

k (segregation coefficient) = 1



to minimize interdiffusion use a low T growth and high growth rates