Anisotropic Wet Etching

Anisotropic etches also available for single crystal Si:

- Orientation-dependent etching: <111>-plane more densely packed than <100>-plane

Faster E.R.

Slower E.R.

…in some solvents

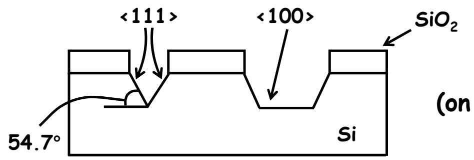
One such solvent: KOH + isopropyl alcohol

(e.g., 23.4 wt% KOH, 13.3 wt% isopropyl alcohol, 63 wt% H_2O)

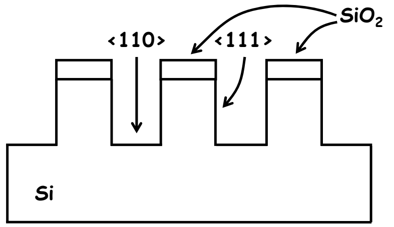
$\Longrightarrow$ $E.R._{<100>} = 100 \times E.R._{<111>}$

Anisotropic Wet Etching (cont.)

Can get the following:



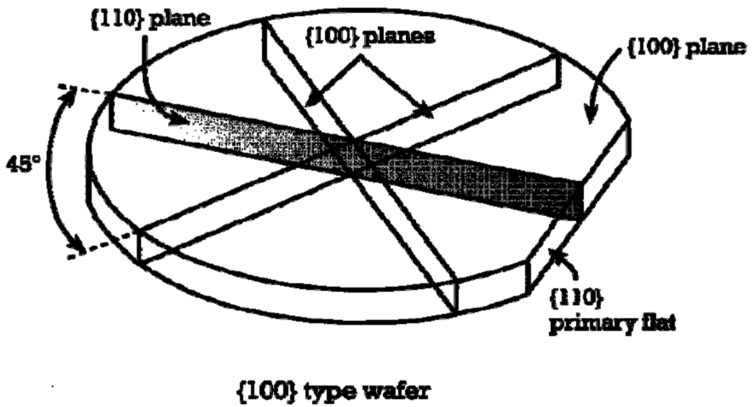
(on a <100> - wafer)



(on a <110> - wafer)

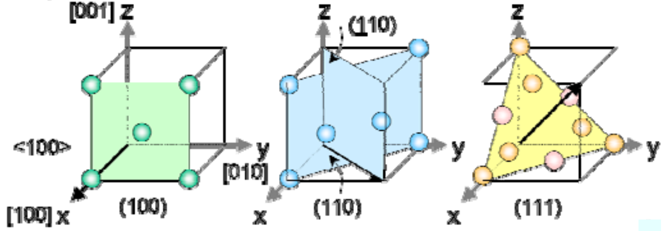
$\Longrightarrow$ Quite anisotropic!

Silicon Wafers



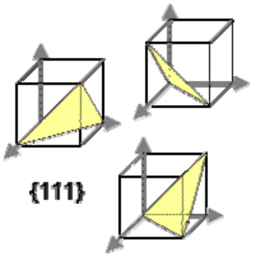
[Maluf]

Silicon Crystallography

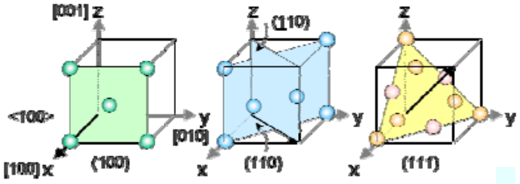


Miller Indices (h k l):

- Planes
  - Reciprocal of plane intercepts with axes
  - e.g., for (110), intercepts: (x,y,z) = (1,1,∞); reciprocals: (1,1,0) → (110)
  - (unique), {family}
- Directions
  - One endpoint of vector @ origin
  - [unique], <family>



Determining Angles Between Planes



- The angle between vectors [abc] and [xyz] is given by:

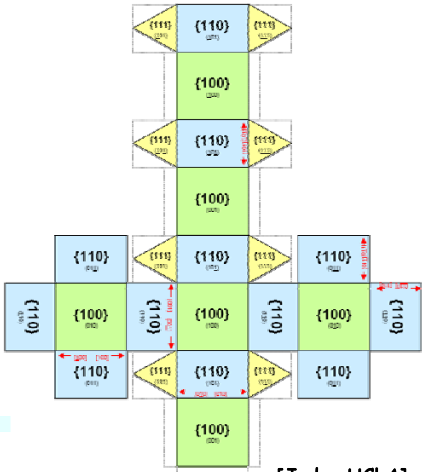
$$ax + by + cz = |(a,b,c)| \cdot |(x,y,z)| \cdot \cos\theta$$

$$\theta_{(a,b,c),(x,y,z)} = \cos^{-1}\left[\frac{ax + by + cz}{|(a,b,c)| \cdot |(x,y,z)|}\right]$$

- For {100} and {110} → 45°
- For {100} and {111} → 54.74°
- For {110} and {111} → 35.26°, 90°, and 144.74°

Silicon Crystal Origami

- Silicon fold-up cube
- Adapted from Profs. Kris Pister and Jack Judy
- Print onto transparency
- Assemble inside out
- Visualize crystal plane orientations, intersections, and directions

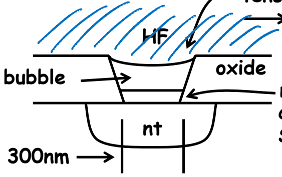


[Judy, UCLA]

Wet Etching SiO_2

$$SiO_2 + 6HF \longrightarrow H_2 + SiF_6 + 2H_2O$$

Generally used to clear out residual oxides from contacts



Problem: Contact hole is so thin that surface tensions don't allow the HF to get into the contact → Generally the case for VLSI circuits

native oxide can get this just by exposing Si to air → 1-2nm-thick

Solution: add a surfactant (e.g., Triton X) to the BHF before the contact clear etch

1. Improves the ability of HF to wet the surface (hence, get into the contact)
2. Suppresses the formation of etch by-products, which otherwise can block further reaction if by-products get caught in the contact

More Wet Etch Chemistries

- Wet etching silicon nitride
  - Use hot phosphoric acid: 85% phosphoric acid @ 180°C
  - Etch rate ~ 10 nm/min (quite slow)
  - Problem: PR lifted during such etching
  - Solution: use SiO_2 as an etch mask (E.R. ~2.5 nm/min)
    - A hassle → dry etch processes more common than wet
- Wet etchining aluminum
  - Typical etch solution composition:

80% phoshporic acid, 5% nitric acid, 5% acetic acid, 10% water

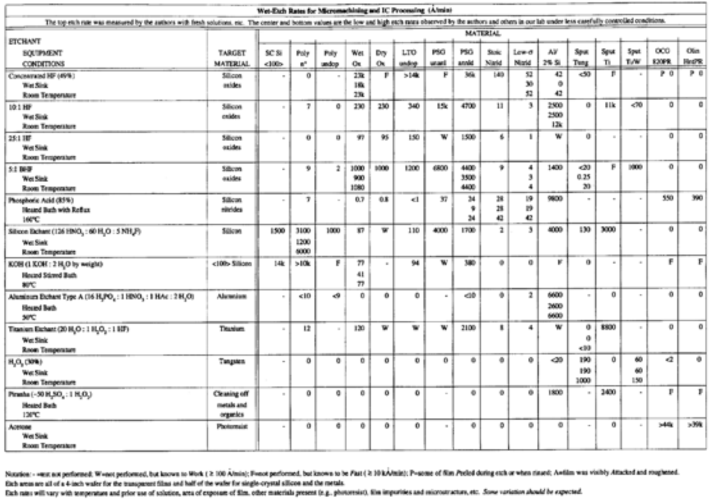
(H_3PO_4) (HNO_3) (CH_3COOH) (H_2O)

(1) Forms Al_2O_3 (aluminum oxide)

(2) Dissolves the Al_2O_3

  - Problem: H_2 gas bubbles adhere firmlly to the surface → delay the etch → need a 10-50% overetch time
  - Solution: mechanical agitation, periodic removal of wafers from etching solution

Wet Etch Rates (f/ K. Williams)



Film Etch Chemistries

- For some popular films:

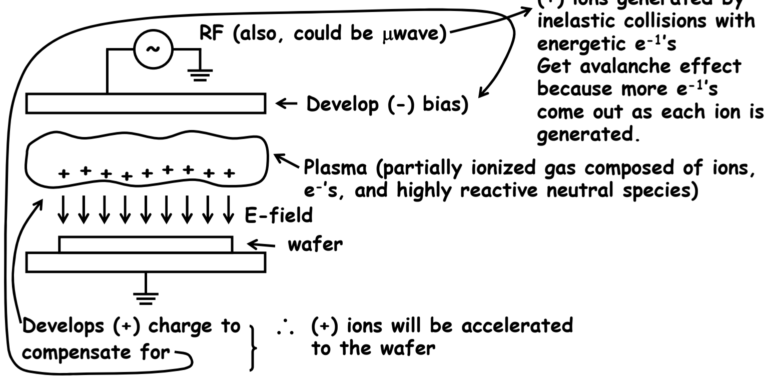
Material	Wet etchant	Etch rate [nm/min]	Dry etchant	Etch rate [nm/min]
Polysilicon	HNO_3:H_2O:NH_4F	120-600	SF_6 + He	170-920
Silicon nitride	H_3PO_4	5	SF_6	150-250
Silicon dioxide	HF	20-2000	CHF_3 + O_2	50-150
Aluminum	H_3PO_4:HNO_3:CH_3COOH	660	Cl_2 + $SiCl_4$	100-150
Photoresist	Acetone	>4000	O_2	35-3500
Gold	KI	40	n/a	n/a

Dry Etching

Dry Etching

- Physical sputtering
- Plasma etching
- Reactive ion etching

} All based upon plasma processes.



RF (also, could be μwave)

(+) ions generated by inelastic collisions with energetic e^{-1}'s

Get avalanche effect because more e^{-1}'s come out as each ion is generated.

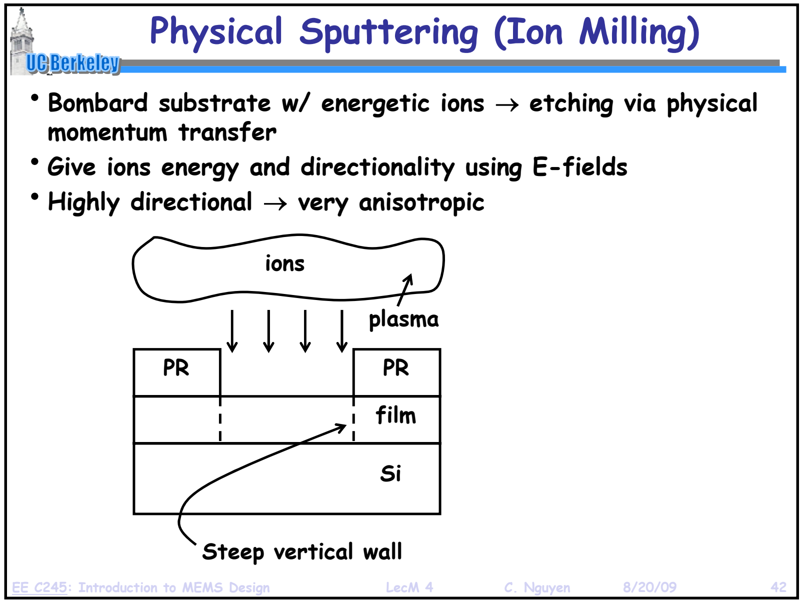
← Develop (−) bias)

Plasma (partially ionized gas composed of ions, e^{-}'s, and highly reactive neutral species)

E-field

wafer

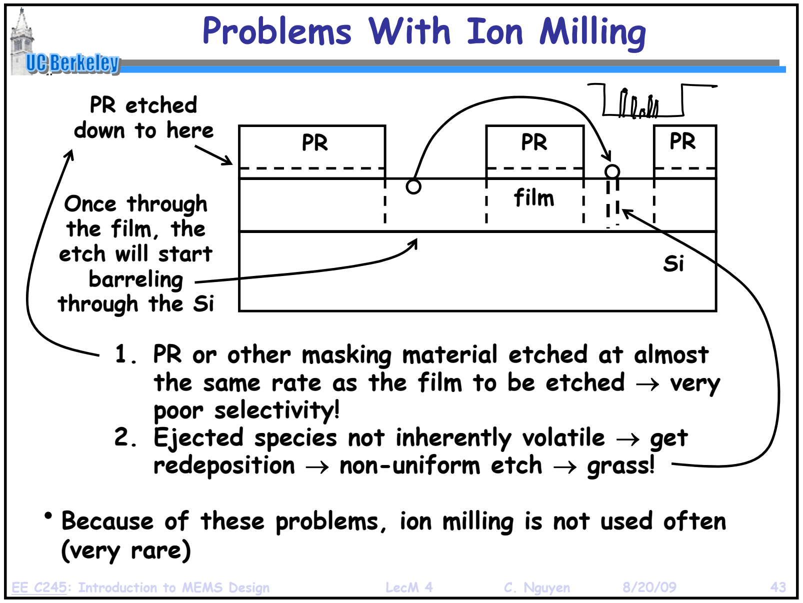
Develops (+) charge to compensate for } ∴ (+) ions will be accelerated to the wafer



Physical Sputtering (Ion Milling)

- Bombard substrate w/ energetic ions → etching via physical momentum transfer
- Give ions energy and directionality using E-fields
- Highly directional → very anisotropic

Steep vertical wall



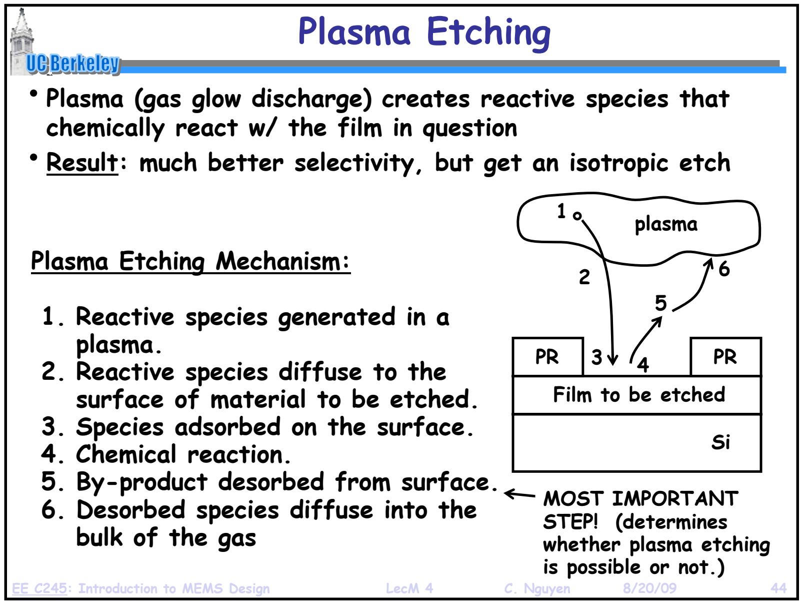
Problems With Ion Milling

PR etched down to here

Once through the film, the etch will start barreling through the Si

1. PR or other masking material etched at almost the same rate as the film to be etched → very poor selectivity!
2. Ejected species not inherently volatile → get redeposition → non-uniform etch → grass!

- Because of these problems, ion milling is not used often (very rare)



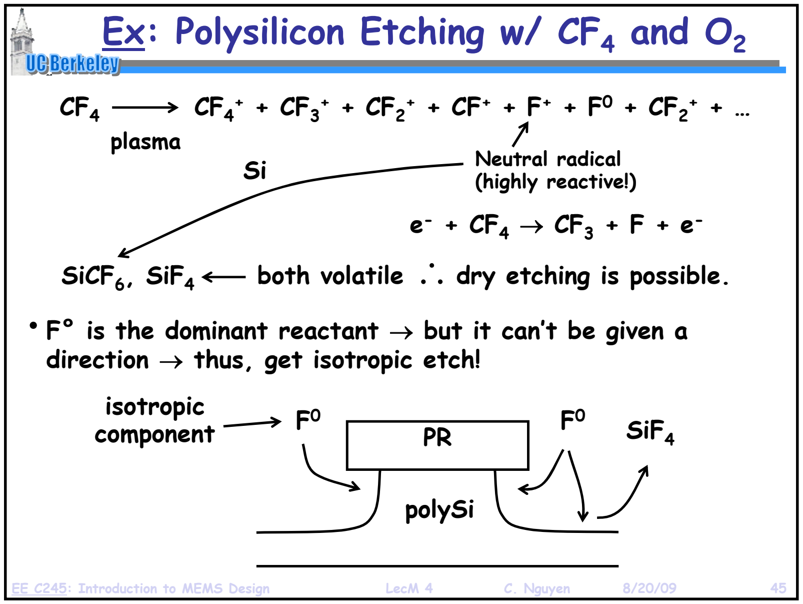
Plasma Etching

- Plasma (gas glow discharge) creates reactive species that chemically react w/ the film in question
- Result: much better selectivity, but get an isotropic etch

Plasma Etching Mechanism:

1. Reactive species generated in a plasma.
2. Reactive species diffuse to the surface of material to be etched.
3. Species adsorbed on the surface.
4. Chemical reaction.
5. By-product desorbed from surface.
6. Desorbed species diffuse into the bulk of the gas

MOST IMPORTANT STEP! (determines whether plasma etching is possible or not.)



Ex: Polysilicon Etching w/ CF_4 and O_2

$$CF_4 \xrightarrow[\text{plasma}]{} CF_4^+ + CF_3^+ + CF_2^+ + CF^+ + F^+ + F^0 + CF_2^+ + \ldots$$

Si

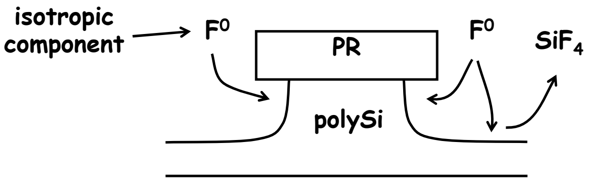
Neutral radical (highly reactive!)

$$e^- + CF_4 \rightarrow CF_3 + F + e^-$$

$SiCF_6$, SiF_4 ← both volatile ∴ dry etching is possible.

- F^0 is the dominant reactant → but can't be given a direction → thus, get isotropic etch!

Ex: Polysilicon Etching w/ CF_4 and O_2

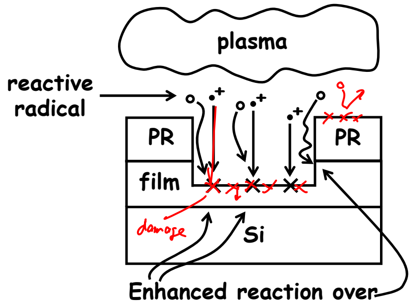


- **Problems**:
  1. Isotropic etching
  2. Formation of polymer because of C in CF_4
     - Solution: add O_2 to remove the polymer (but note that this reduces the selectivity, $S_{poly/PR}$)
- **Solution**:
  - Use Reactive Ion Etching (RIE)

Reactive Ion Etching (RIE)

- Use ion bombardment to aid and enhance reactive etching in a particular direction
  - Result: directional, anisotropic etching!
- RIE is somewhat of a misnomer
  - It's not ions that react … rather, it's still the neutral species that dominate reaction
  - Ions just enhance reaction of these neutral radicals in a specific direction
- Two principle postulated mechanisms behind RIE
  1. Surface damage mechanism
  2. Surface inhibitor mechanism

RIE: Surface Damage Mechanism

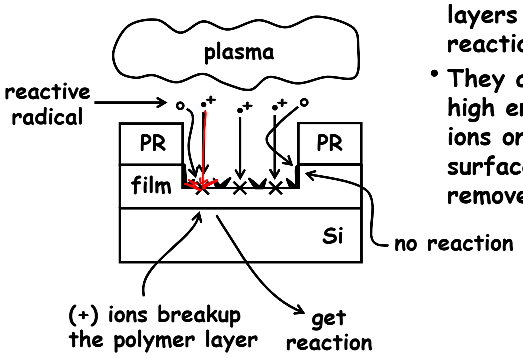


- Relatively high energy impinging ions (>50 eV) produce lattice damage at surface
- Reaction at these damaged sites is enhanced compared to reactions at undamaged areas

Result: E.R. at surface >> E.R. on sidewalls

RIE: Surface Inhibitor Mechanism

- Non-volatile polymer layers are a product of reaction
- They are removed by high energy directional ions on the horizontal surface, but not removed from sidewalls

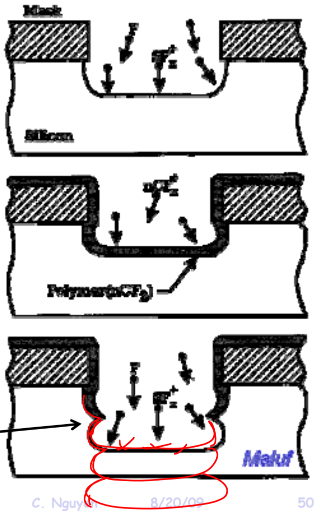


Result: E.R. @ surface >> E.R. on sidewalls

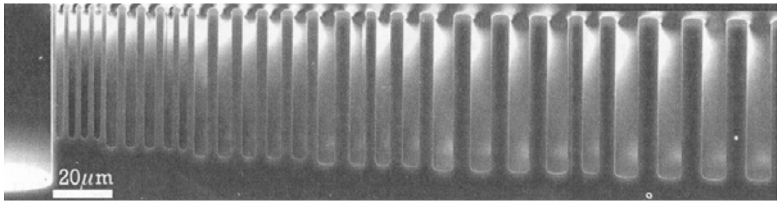
Deep Reactive-Ion Etching (DRIE)

The Bosch process:

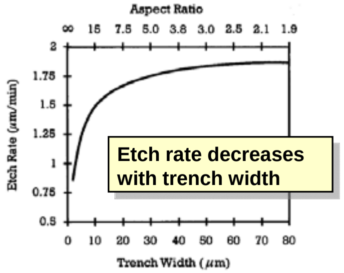
- Inductively-coupled plasma
- Etch Rate: 1.5-4 μm/min
- Two main cycles in the etch:
  - Etch cycle (5-15 s): SF_6 (SF_x^+) etches Si
  - Deposition cycle: (5-15 s): C_4F_8 deposits fluorocarbon protective polymer $(CF_2^-)_n$
- Etch mask selectivity:
  - SiO_2 ~ 200:1
  - Photoresist ~ 100:1
- Issue: finite sidewall roughness
  - scalloping < 50 nm
- Sidewall angle: 90° ± 2°



DRIE Issues: Etch Rate Variance



- Etch rate is diffusion-limited and drops for narrow trenches
  - Adjust mask layout to eliminate large disparities
  - Adjust process parameters (slow down the etch rate to that governed by the slowest feature)

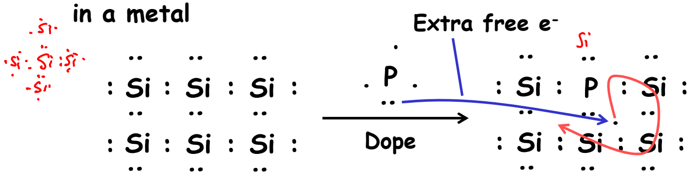


Etch rate decreases with trench width

Semiconductor Doping

Doping of Semiconductors

- Semiconductors are not intrinsically conductive
- To make them conductive, replace silicon atoms in the lattice with dopant atoms that have valence bands with fewer or more e^-'s than the 4 of Si
- If more e^-'s, then the dopant is a donor: P, As
  - The extra e^- is effectively released from the bonded atoms to join a cloud of free e^-'s, free to move like e^-'s in a metal



  - The larger the # of donor atoms, the larger the # of free e^-'s → the higher the conductivity

Doping of Semiconductors (cont.)

- Conductivity Equation:

charge magnitude on an electron

$$\sigma = q\mu_n n + q\mu_p p$$

conductivity

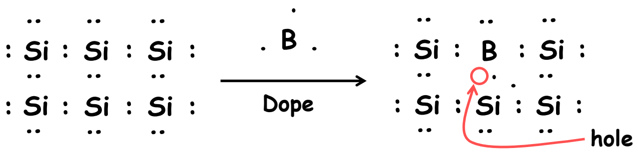
electron mobility

electron density

hole mobility

hole density

- If fewer e⁻'s, then the dopant is an acceptor: B



↳ Lack of an e^- = hole = h^+

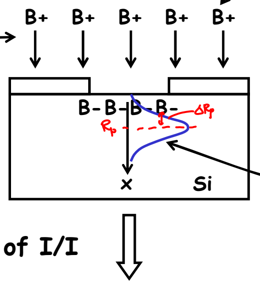
↳ When e^-'s move into h^+'s, the h^+'s effectively move in the opposite direction → a h^+ is a mobile (+) charge carrier

Ion Implantation

Ion Implantation

- Method by which dopants can be introduced in silicon to make the silicon conductive, and for transistor devices, to form, e.g., pn-junctions, source/drain junctions, …

The basic process:



Charged dopant accelerated to high energy by an E-Field (e.g., 100 keV)

Control current & time to control the dose.

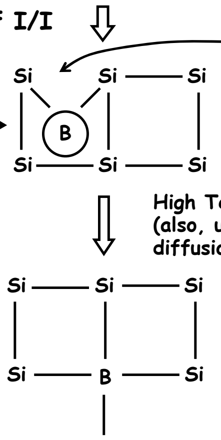
Masking material (could be PR, could be oxide, etc.)

Depth determined by energy & type of dopant

Result of I/I

Ion Implantation (cont.)

Result of I/I



Damage → Si layer at top becomes amorphous

↳ B not in the lattice, so it's not electrically active.

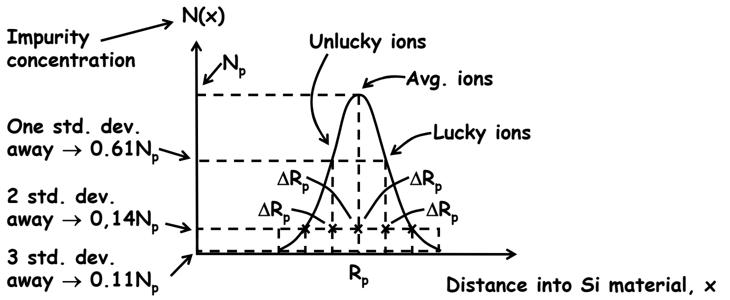
Ion collides with atoms and interacts with e⁻'s in the lattice → all of which slow it down and eventually stop it.

High Temperature Anneal (also, usually do a drive-in diffusion) (800-1200°C)

↳ Now B in the lattice & electrically active! (serves as dopant)

This is a statistical process → implanted impurity profile can be approximated by a Gaussian distribution.

Statistical Modeling of I/I



$R_p \triangleq$ Projected range = avg. distance on ion trends before stopping

$\Delta R_p \triangleq$ Straggle = std. deviation characterizing the spread of the distribution.

Analytical Modeling for I/I

Mathematically:

$$N(x) = N_p \exp\left[-\frac{(x-R_p)^2}{2(\Delta R_p)^2}\right]$$

Area under the impurity distribution curve } Implanted Dose = $Q = \int_0^\infty N(x)dx \ \left[ions/cm^2\right]$

For an implant completely contained within the Si:

$$Q = \sqrt{2\pi} N_p \Delta R_p$$

Assuming the peak is in the silicon: (putting it in one-sided diffusion form) → So we can track the dopant front during a subsequent diffusion step.

$D_I = Q$

$$N(x) = \frac{D_I/2}{\sqrt{\pi (Dt)_{eff}}} \exp\left[-\frac{(x-R_p)^2}{2(\Delta R_p)^2}\right]$$, where $(Dt)_{eff} = \frac{(\Delta R_p)^2}{2}$

I/I Range Graphs

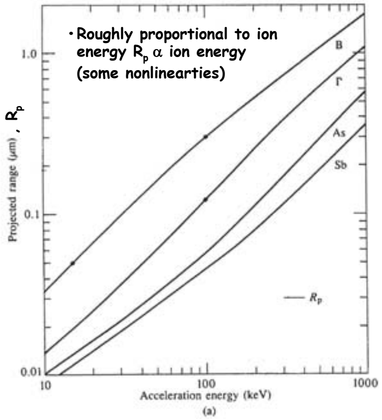


Figure 6.1

- R$_p$ is a function of the energy of the ion and atomic number of the ion and target material
- <u>Lindhand, Scharff and Schiott (LSS) Theory</u>:
- Assumes implantation into amorphous material, i.e, atoms of the target material are randomly positioned
- Yields the curves of Fig. 6.1 and 6.2
- For a given energy, lighter elements strike Si with higher velocity and penetrate more deeply

I/I Straggle Graphs

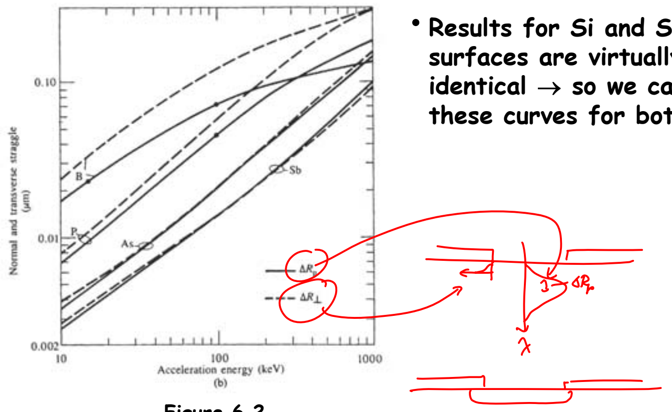


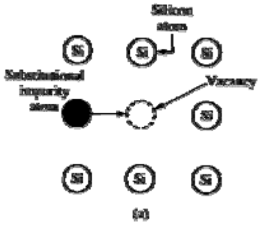
Figure 6.2

- Results for Si and SiO$_2$ surfaces are virtually identical → so we can use these curves for both

Diffusion

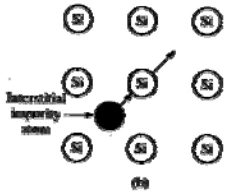
Diffusion in Silicon

- Movement of dopants within the silicon at high temperatures
- Three mechanisms: (in Si)



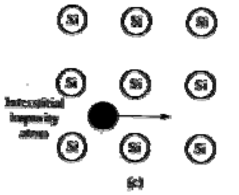
Substitutional Diffusion

- Impurity moves along vacancies in the lattice
- Substitutes for a Si-atom in the lattice



Interstitialcy Diffusion

- Impurity atom replaces a Si atom in the lattice
- Si atom displaced to an interstitial site

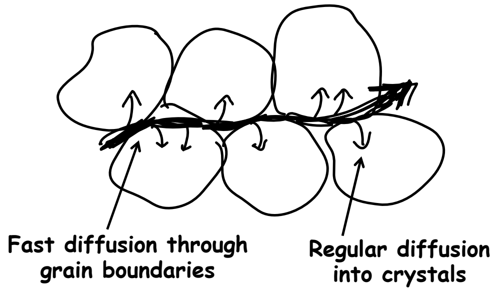


Interstitial Diffusion

- Impurity atoms jump from one interstitial site to another
- Get rapid diffusion
  - ↳ Hard to control
  - ↳ Impurity not in lattice so not electrically active

Diffusion in Polysilicon

- In polysilicon, still get diffusion into the crystals, but get more and faster diffusion through grain boundaries
- **Result**: overall faster diffusion than in silicon

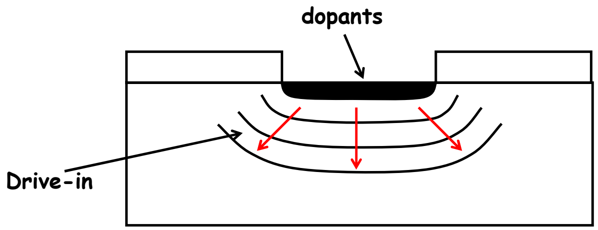


- In effect, larger surface area allows much faster volumetric diffusion

Basic Process for Selective Doping

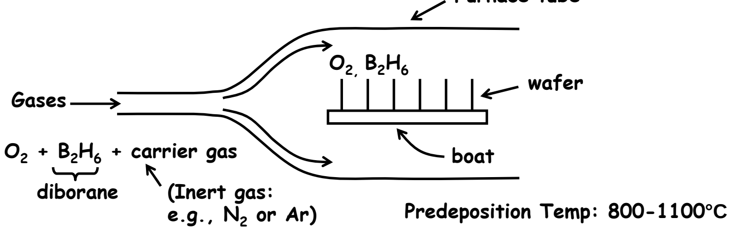
1. Introduce dopants (introduce a fixed dose Q of dopants)
   (i) Ion implantation
   (ii) Predeposition
2. Drive in dopants to the desired depth
   ↳ High temperature > 900°C in N_2 or N_2/O_2

- **Result**:



Predeposition

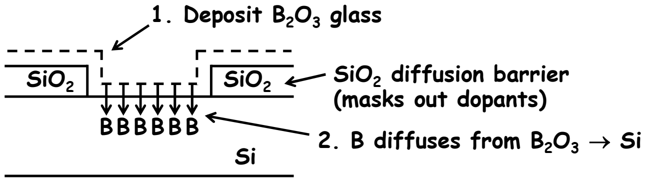
- Furnace-tube system using solid, liquid, or gaseous dopant sources
- Used to introduced a controlled amount of dopants
  - Unfortunately, not very well controlled
  - Dose (Q) range: 10^{13} – 10^{16} ± 20%
  - For ref: w/ ion implantation: 10^{11} – 10^{16} ± 1% (larger range & more accurate)
- Example: Boron predeposition



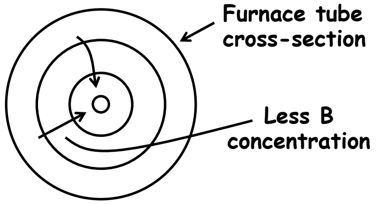
Predeposition Temp: 800-1100°C

Ex: Boron Predeposition

- Basic Procedure:

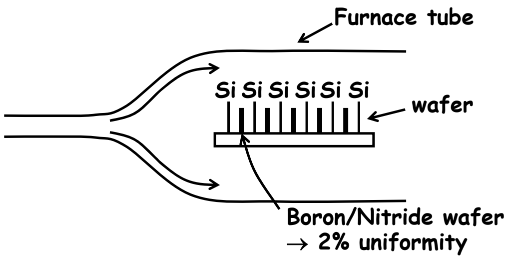


- Difficult to control dose Q, because it's heavily dependent on partial pressure of B_2H_6 gas flow
  - this is difficult to control itself
  - get only 10% uniformity



Ex: Boron Predeposition (cont.)

For better uniformity, use solid source:



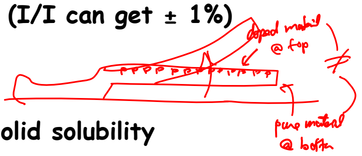
Reactions:

$B_2H_6 + 3O_2 \rightarrow 3H_2O + B_2O_3$

$Si + O_2 \rightarrow SiO_2$

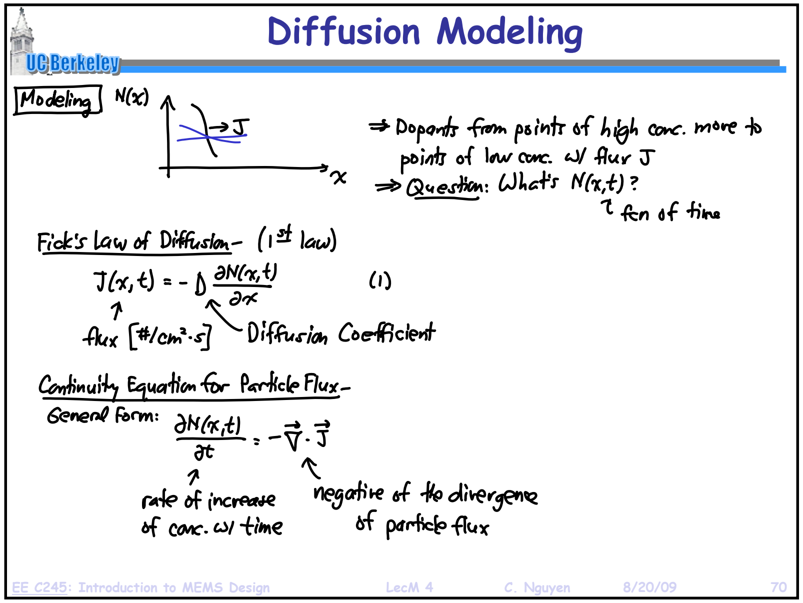
General Comments on Predeposition

- Higher doses only: Q = 10^{13} – 10^{16} cm^{-2} (I/I is 10^{11} – 10^{16})
- Dose not well controlled: ± 20% (I/I can get ± 1%)
- Uniformity is not good
  - ± 10% w/ gas source
  - ± 2% w/ solid source



- Max. conc. possible limited by solid solubility
  - Limited to ~10^{20} cm^{-3}
  - No limit for I/I → you force it in here!

- For these reasons, I/I is usually the preferred method for introduction of dopants in transistor devices
- But I/I is not necessarily the best choice for MEMS
  - I/I cannot dope the underside of a suspended beam
  - I/I yields one-sided doping → introduces unbalanced stress → warping of structures
  - I/I can do physical damage → problem if annealing is not permitted
- Thus, predeposition is often preferred when doping MEMS



Diffusion Modeling

⇒ Dopants from points of high conc. move to points of low conc. w/ flux J

⇒ Question: What's $N(x,t)$?
↖ fcn of time

Fick's Law of Diffusion – (1st law)

$$J(x,t) = -D\frac{\partial N(x,t)}{\partial x} \qquad (1)$$

flux [#/cm²·s] ↗ Diffusion Coefficient

Continuity Equation for Particle Flux –

General Form: $\frac{\partial N(x,t)}{\partial t} = -\vec{\nabla}\cdot\vec{J}$

rate of increase of conc. w/ time; negative of the divergence of particle flux

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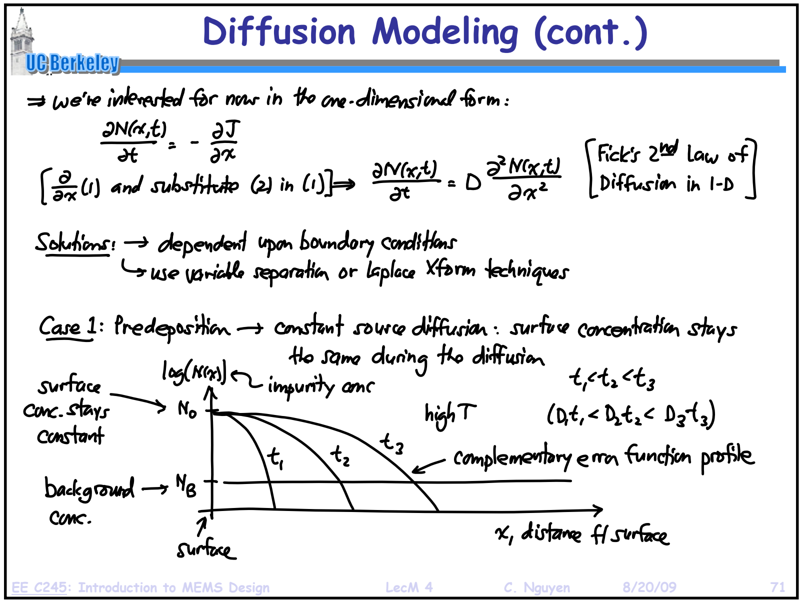

Diffusion Modeling (cont.)

⇒ we're interested for now in the one-dimensional form:

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

$$\left[\frac{\partial}{\partial x}(1) \text{ and substitute (2) in (1)}\right] \Rightarrow \frac{\partial N(x,t)}{\partial t} = D\frac{\partial^2 N(x,t)}{\partial x^2} \quad \left[\begin{array}{l}\text{Fick's 2nd Law of}\\ \text{Diffusion in 1-D}\end{array}\right]$$

Solutions: → dependent upon boundary conditions
↳ use variable separation or laplace Xform techniques

Case 1: Predeposition → constant source diffusion: surface concentration stays the same during the diffusion

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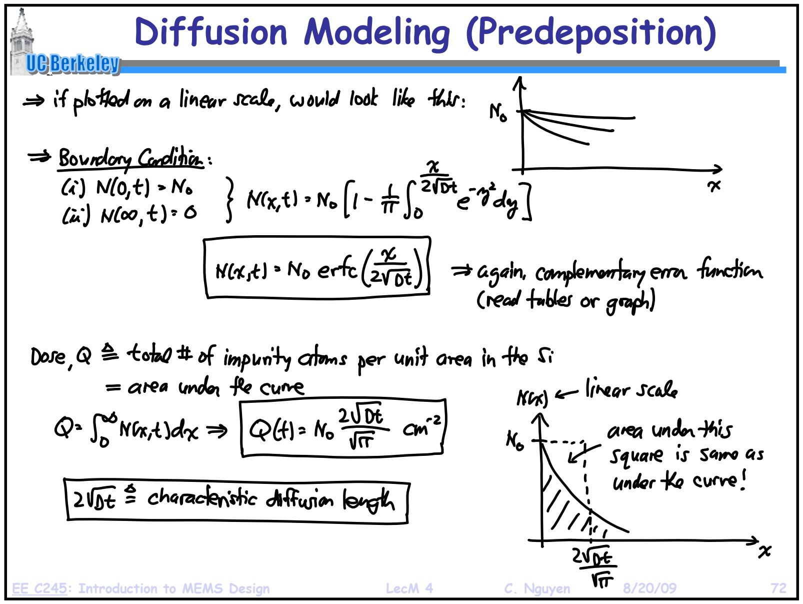

Diffusion Modeling (Predeposition)

⇒ if plotted on a linear scale, would look like this:

⇒ Boundary Condition:

(i) $N(0,t) = N_0$
(ii) $N(\infty,t) = 0$

$$\left.\begin{array}{l} \\ \end{array}\right\} N(x,t) = N_0\left[1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2}dy\right]$$

$$\boxed{N(x,t) = N_0\,\mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)}$$

⇒ again, complementary error function (read tables or graph)

Dose, $Q \triangleq$ total # of impurity atoms per unit area in the Si
= area under the curve

$$Q = \int_0^\infty N(x,t)dx \Rightarrow \boxed{Q(t) = N_0\frac{2\sqrt{Dt}}{\sqrt{\pi}}\ \text{cm}^{-2}}$$

$$\boxed{2\sqrt{Dt} \triangleq \text{characteristic diffusion length}}$$

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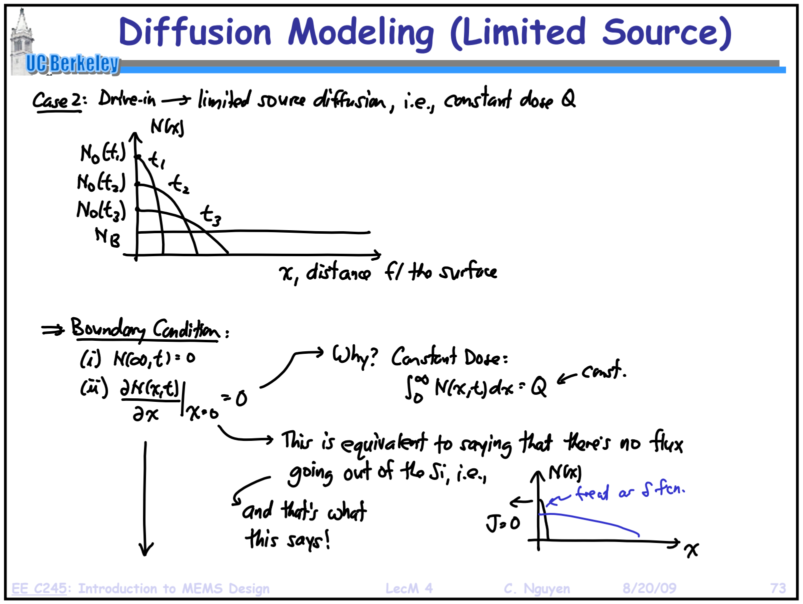

Diffusion Modeling (Limited Source)

Case 2: Drive-in → limited source diffusion, i.e., constant dose Q

⇒ Boundary Condition:

(i) $N(\infty,t) = 0$

(ii) $\left.\frac{\partial N(x,t)}{\partial x}\right|_{x=0} = 0$

→ Why? Constant Dose:
$\int_0^\infty N(x,t)dx = Q$ ← const.

→ This is equivalent to saying that there's no flux going out of the Si, i.e.,

and that's what this says!

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Diffusion Modeling (Limited Source)

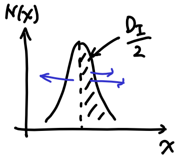
(iii) Usually make delta fcn. approx.: $N(x,0) = Q\delta(x)$

⇒ we can do this, because for sufficiently long diffusion times, no matter what the original shape of the dopant distribution, the diffused distribution will be the same

Get Gaussian Distribution:

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

corresponds to a half Gaussian in this equation



when the starting conc. profile is completely contained in the Si, then

$Q = \frac{D_I}{2}$ = half the implant dose

Two-Step Diffusion

- Two step diffusion procedure:
  - **Step 1**: predeposition (i.e., constant source diffusion)
  - **Step 2**: drive-in diffusion (i.e., limited source diffusion)
- For processes where there is both a predeposition and a drive-in diffusion, the final profile type (i.e., complementary error function or Gaussian) is determined by which has the much greater Dt product:

$(Dt)_{predep} \gg (Dt)_{drive\text{-}in}$ ⇨ impurity profile is complementary error function

$(Dt)_{drive\text{-}in} \gg (Dt)_{predep}$ ⇨ impurity profile is Gaussian (which is usually the case)

Successive Diffusions

- For actual processes, the junction/diffusion formation is only one of many high temperature steps, each of which contributes to the final junction profile
- Typical overall process:
  1. Selective doping
     - Implant → effective $(Dt)_1 = (\Delta R_p)^2/2$ (Gaussian)
     - Drive-in/activation → D_2t_2
  2. Other high temperature steps
     - (eg., oxidation, reflow, deposition) → D_3t_3, D_4t_4, …
     - Each has their own Dt product
  3. Then, to find the final profile, use

temperature

time

$$(Dt)_{tot} = \sum_i D_i t_i$$

in the Gaussian distribution expression.

The Diffusion Coefficient

$$D = D_o \exp\left(-\frac{E_A}{kT}\right)$$

(as usual, an Arrhenius relationship)

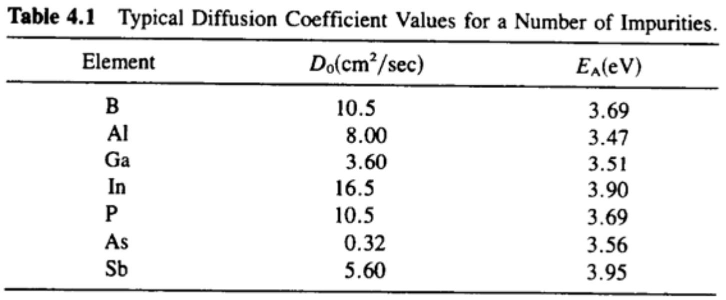


Table 4.1 Typical Diffusion Coefficient Values for a Number of Impurities.

Element	D_0(cm²/sec)	E_A(eV)
B	10.5	3.69
Al	8.00	3.47
Ga	3.60	3.51
In	16.5	3.90
P	10.5	3.69
As	0.32	3.56
Sb	5.60	3.95

Diffusion Coefficient Graphs

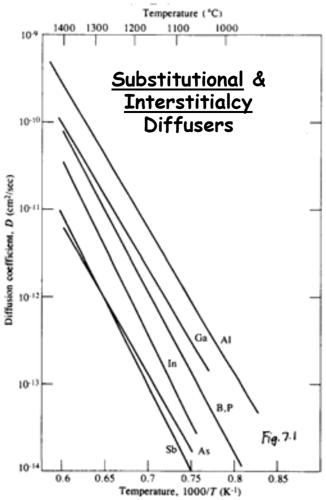


Fig. 7.1

Interstitial Diffusers

↳ Note the much higher diffusion coeffs. than for substitutional

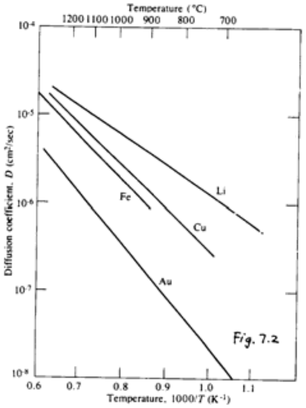
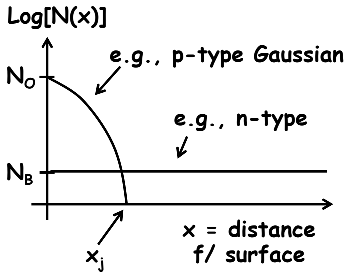
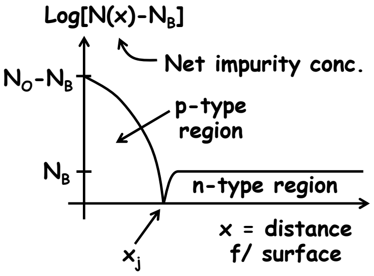


Fig. 7.2

Metallurgical Junction Depth, x_j

x_j = point at which diffused impurity profile intersects the background concentration, N_B





Expressions for x_j

- Assuming a Gaussian dopant profile: (the most common case)

$$N(x_j,t) = N_o \exp\left[-\left(\frac{x_j}{2\sqrt{Dt}}\right)^2\right] = N_B \quad\rightarrow\quad x_j = 2\sqrt{Dt\ln\left(\frac{N_o}{N_B}\right)}$$

- For a complementary error function profile:

$$N(x_j,t) = N_o \operatorname{erfc}\left(\frac{x_j}{2\sqrt{Dt}}\right) = N_B \quad\rightarrow\quad x_j = 2\sqrt{Dt}\operatorname{erfc}^{-1}\left(\frac{N_B}{N_o}\right)$$

Sheet Resistance

- Sheet resistance provides a simple way to determine the resistance of a given conductive trace by merely counting the number of effective squares
- **Definition**:

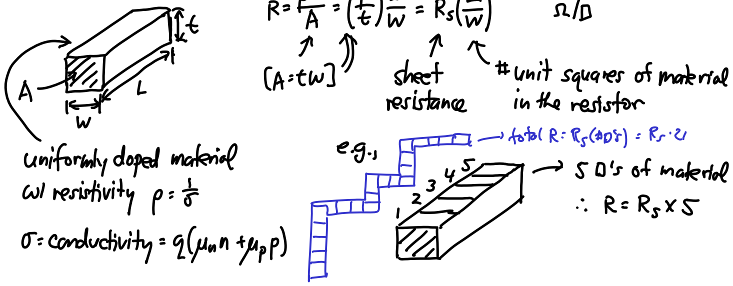
ohms per square

$$R = \frac{\rho L}{A} = \left(\frac{\rho}{t}\right)\frac{L}{W} = R_s\left(\frac{L}{W}\right) \qquad \Omega/\square$$

[A=tW]

sheet resistance

unit squares of material in the resistor



uniformly doped material w/ resistivity $\rho = \frac{1}{\sigma}$

σ = conductivity = $q(\mu_n n + \mu_p p)$

e.g.,

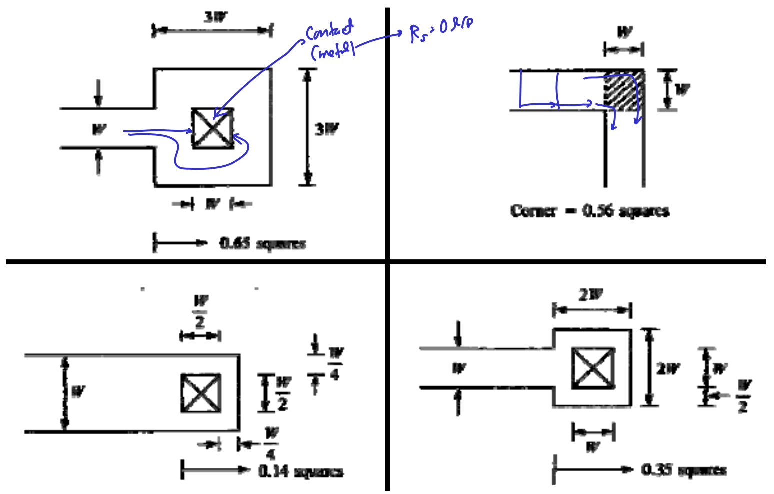
total R = R_s(#□'s) = $R_s \cdot 21$

5 □'s of material

∴ R = R_s × 5

- What if the trace is non-uniform? (e.g., a corner, contains a contact, etc.)

Squares From Non-Uniform Traces



Sheet Resistance of a Diffused Junction

- For diffused layers:

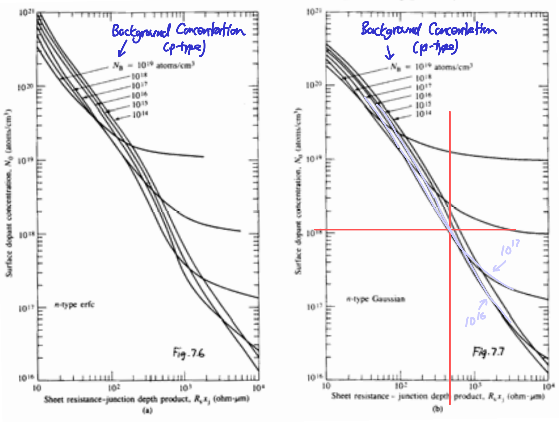
Sheet resistance; Effective resistivity; Majority carrier mobility; Net impurity concentration

$$R_s = \frac{\overline{\rho}}{x_j} = \left[\int_o^{x_j} \sigma(x)dx\right]^{-1} = \left[\int_o^{x_j} q\mu N(x)dx\right]^{-1}$$

[extrinsic material]

- This expression neglects depletion of carriers near the junction, x_j → thus, this gives a slightly lower value of resistance than actual
- Above expression was evaluated by Irvin and is plotted in "Irvin's curves" on next few slides
  - ↳ Illuminates the dependence of R_s on x_j, N_o (the surface concentration), and N_B (the substrate background conc.)

Irvin's Curves (for n-type diffusion)



Example.
Given: p-type
N_B = 3x10^{16} cm^{-3}
N_o = 1.1x10^{18} cm^{-3}
(n-type Gaussian)
x_j = 2.77 μm
Can determine these given known predep. and drive conditions

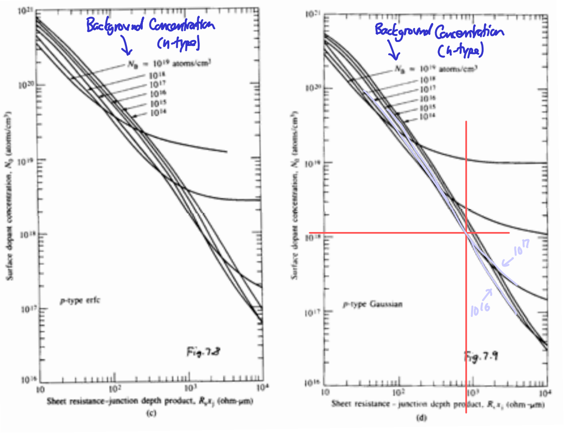
Determine the R_s.

Using Fig. 7.7:

$R_s x_j = 470\,\Omega\cdot\mu m$

$\therefore R_s = \frac{470}{2.77} = \underline{170\,\Omega/\square}$

Irvin's Curves (for p-type diffusion)



Example.
Given: n-type
N_B = 3x10^{16} cm^{-3}
N_o = 1.1x10^{18} cm^{-3}
(p-type Gaussian)
x_j = 2.77 μm
Can determine these given known predep. and drive conditions

Determine the R_s.

Using Fig. 7.9:

$R_s x_j = 800\,\Omega\cdot cm$

$\therefore R_s = \frac{800}{2.77} = 289\,\Omega/\square$