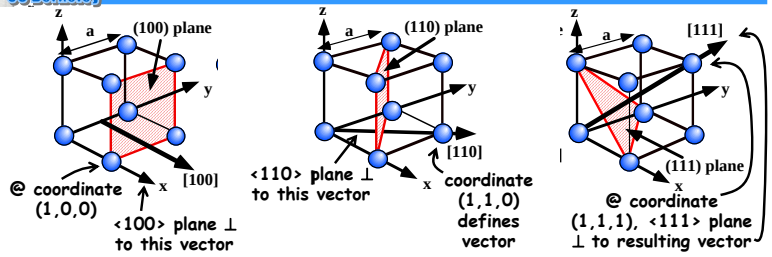
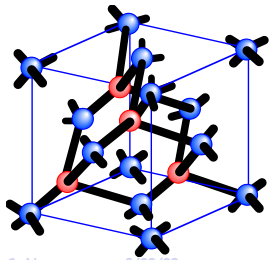
## Silicon Crystal Orientation




- Silicon has the basic diamond structure
  - Two merged FCC cells offset by (a/4) in x, y, and z axes
  - From right:
    - # available bonds/cm$^2$ <111>
    - # available bonds/cm$^2$ <110>
    - # available bonds/cm$^2$ <100>

Increasing ↑





## 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

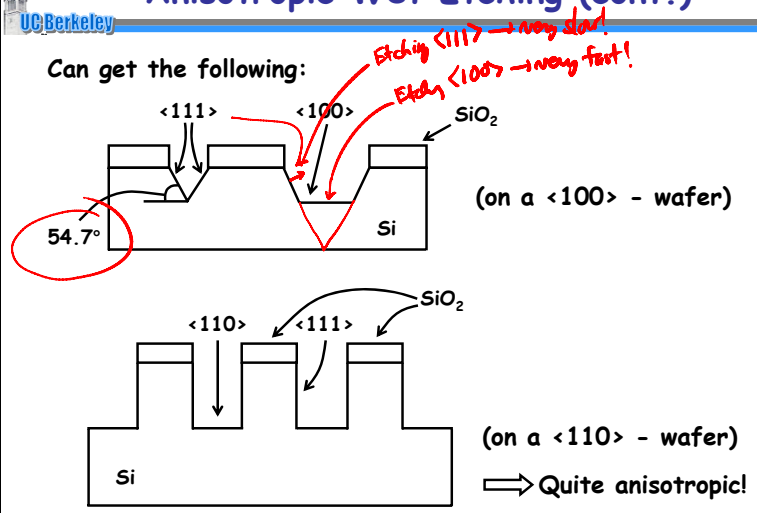
(e.g., 23.4 wt% KOH, 13.3 wt% isopropyl alcohol, 63 wt% $H_2O$)

$\Rightarrow$ E.R.$_{<100>}$ = 100 x E.R.$_{<111>}$



## Anisotropic Wet Etching (cont.)

Can get the following:

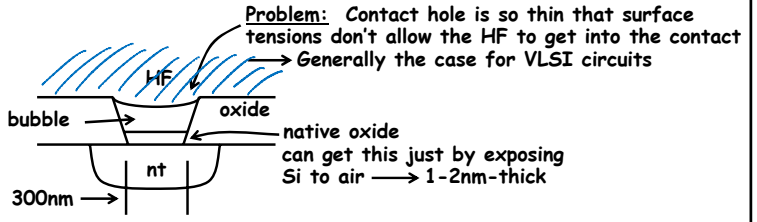





## Wet Etching $SiO_2$

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

Generally used to clear out residual oxides from contacts




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

$(H_2PO_4)$ $(HNO_3)$ $(CH_3COOH)$ $(H_2O)$

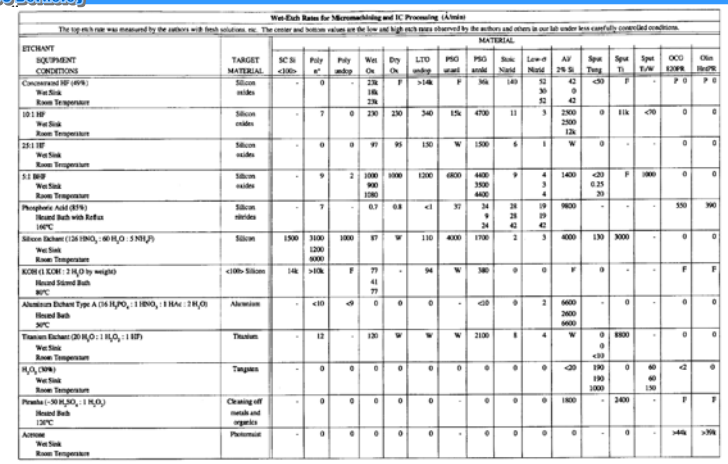
(1) Forms $Al_2O_3$ (aluminum oxide)

(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)



Wet-Etch Rates for Micromachining and IC Processing (A/min)

The top etch rate was measured by the authors with fresh solutions, etc. The center and bottom values are the low and high etch rates observed by the authors and others in our lab under less carefully controlled conditions.

| ETCHANT EQUIPMENT CONDITIONS | TARGET MATERIAL | MATERIAL: SC Si <100> | Poly n+ | Poly undop | Wet Ox | Dry Ox | LTO undop | PSG unanl | PSG anneal | Stoic. Nitrid | Low-st Nitrid | Al/ 2% Si | Sputt Tung | Sputt Ti | Sputt Ti/W | OCG 820FR | Olin Hnt7R |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Concentrated HF (49%)<br>Wet Sink<br>Room Temperature | Silicon oxides | - | 0 | - | 23k<br>18k<br>23k | F | >14k | F | 36k | 140 | 52<br>30<br>52 | 42<br>0<br>42 | <50 | F | - | P 0 | P 0 |
| 10:1 HF<br>Wet Sink<br>Room Temperature | Silicon oxides | - | 7 | 0 | 230 | 230 | 240 | 15k | 4700 | 11 | 3 | 2500<br>2500<br>12k | 0 | 11k | <70 | 0 | 0 |
| 25:1 HF<br>Wet Sink<br>Room Temperature | Silicon oxides | - | 0 | 0 | 97 | 95 | 150 | W | 1500 | 6 | 1 | W | 0 | - | - | 0 | 0 |
| 5:1 BHF<br>Wet Sink<br>Room Temperature | Silicon oxides | - | 9 | 2 | 1000<br>900<br>1080 | 1000 | 1200 | 6800 | 6400<br>3500<br>6400 | 9 | 4<br>3<br>4 | 1400 | <20<br>0.25<br>20 | F | 1000 | 0 | 0 |
| Phosphoric Acid (85%)<br>Heated Bath with Reflux<br>160°C | Silicon nitrides | - | 7 | - | 0.7 | 0.8 | <1 | 37 | 24<br>9<br>24 | 28<br>28<br>42 | 19<br>19<br>42 | 9800 | - | - | - | 550 | 390 |
| Silicon Etchant (126 $HNO_3$ : 60 $H_2O$ : 5 $NH_4F$)<br>Wet Sink<br>Room Temperature | Silicon | 1500 | 3100<br>1200<br>6000 | 1000 | 87 | W | 110 | 4000 | 1700 | 2 | 3 | 4000 | 130 | 3000 | - | 0 | 0 |
| KOH (1 KOH : 2 $H_2O$ by weight)<br>Heated Stirred Bath<br>80°C | <100> Silicon | 14k | >10k | F | 77<br>41<br>77 | - | 94 | W | 380 | 0 | 0 | F | 0 | - | - | F | F |
| Aluminum Etchant Type A (16 $H_3PO_4$ : 1 $HNO_3$ : 1 HAc : 2 $H_2O$)<br>Heated Bath<br>36°C | Aluminum | - | <10 | <9 | 0 | 0 | 0 | - | <10 | 0 | 2 | 6600<br>2600<br>6600 | - | 0 | - | 0 | 0 |
| Titanium Etchant (20 $H_2O$ : 1 $H_2O_2$ : 1 HF)<br>Wet Sink<br>Room Temperature | Titanium | - | 12 | - | 120 | W | W | W | 2100 | 8 | 4 | W | 0<br>0<br><10 | 8800 | - | 0 | 0 |
| $H_2O_2$ (30%)<br>Wet Sink<br>Room Temperature | Tungsten | - | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | <20 | 190<br>190<br>1000 | 0 | 60<br>60<br>130 | <2 | 0 |
| Piranha (~50 $H_2SO_4$ : 1 $H_2O_2$)<br>Heated Bath<br>120°C | Cleaning off metals and organics | - | 0 | 0 | 0 | 0 | 0 | - | 0 | 0 | 0 | 1800 | - | 2400 | - | F | F |
| Acetone<br>Wet Sink<br>Room Temperature | Photoresist | - | 0 | 0 | 0 | 0 | 0 | - | 0 | 0 | 0 | 0 | - | 0 | - | >44k | >39k |

Notation: - =not not performed. W=not performed, but known to Work (≥ 100 A/min); F=not performed, but known to be Fast (≥ 10 kA/min); P=some of film Peeled during etch or when rinsed; Asl=film was visibly Attacked and roughened.
Each areas are all of a 4-inch wafer for the transparent films and half of the wafer for single-crystal silicon and the metals.
Each rate will vary with temperature and prior use of solution, area of exposure of film, other materials present (e.g. photoresist), film impurities and microstructure, etc. *Some variation should be expected.*



## 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 |

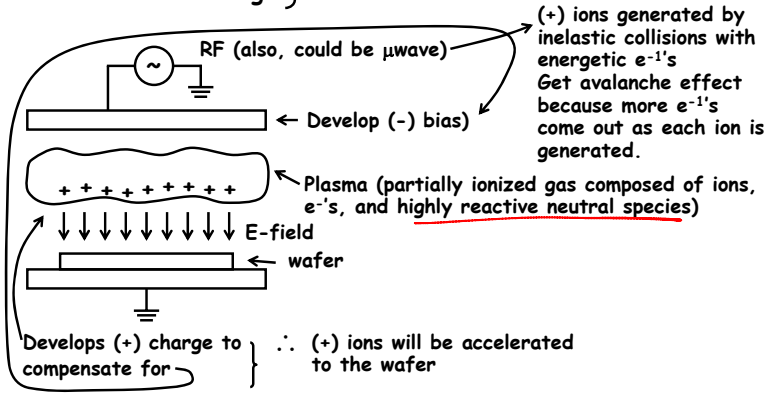


## Dry Etching

## Dry Etching

- Physical sputtering
- Plasma etching
- Reactive ion etching

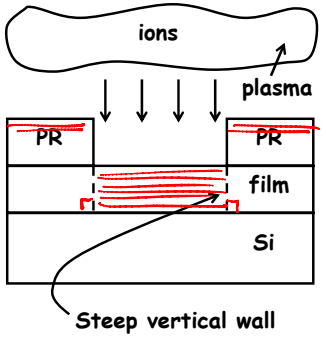
} All based upon plasma processes.





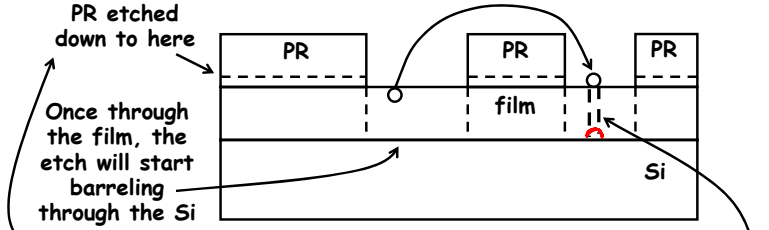

## Physical Sputtering (Ion Milling)

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






## Problems With Ion Milling



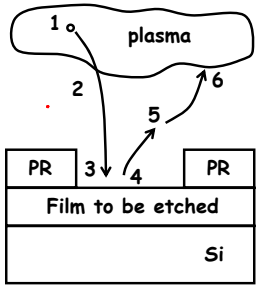

1. PR or other masking material etched at almost the same rate as the film to be etched → very poor selectivity!
2. Ejected species not inherently volatile → get redeposition → non-uniform etch → grass!

- 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. ← MOST IMPORTANT STEP! (determines whether plasma etching is possible or not.)
6. Desorbed species diffuse into the bulk of the gas

## Ex: Polysilicon Etching w/ $CF_4$ and $O_2$

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

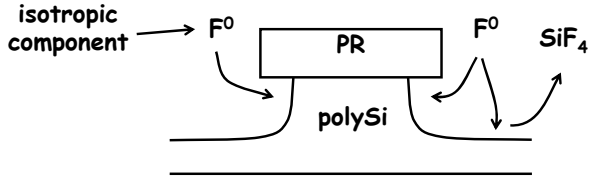
Neutral radical (highly reactive!)

Si

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

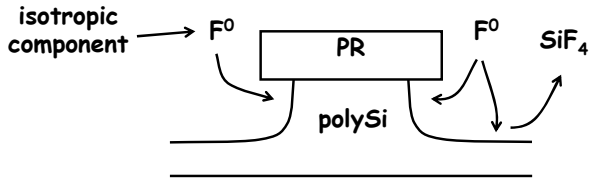
$SiCF_6$, $SiF_4$ ← both volatile ∴ dry etching is possible.

- F° is the dominant reactant → but it 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)

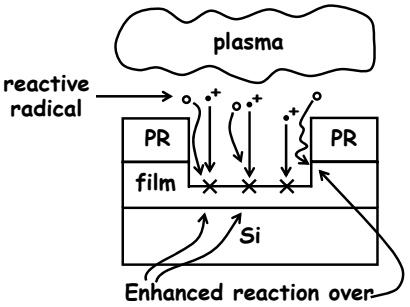


## Reactive Ion Etching (RIE)

- 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



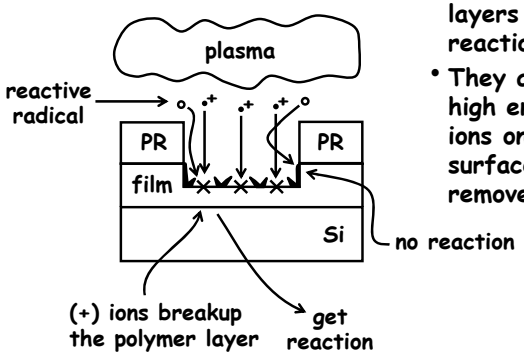
## RIE: Surface Damage Mechanism




- 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

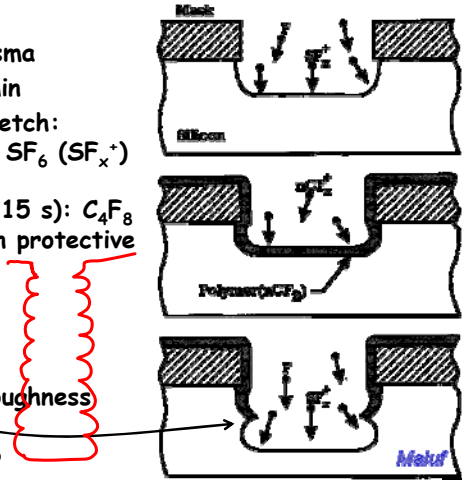
Result: E.R. @ surface >> E.R. on sidewalls



## Deep Reactive-Ion Etching (DRIE)

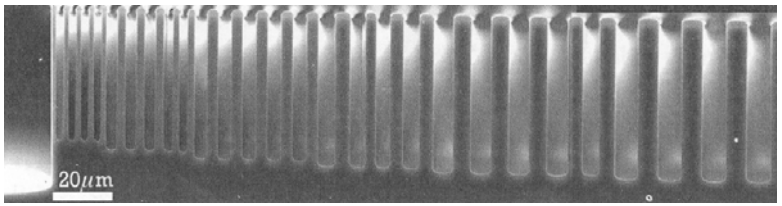
The Bosch process:

- 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°

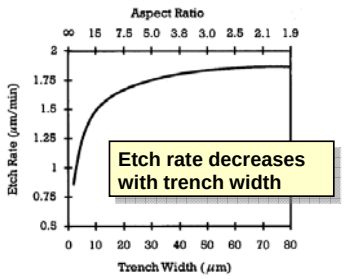





## DRIE Issues: Etch Rate Variance




- 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)

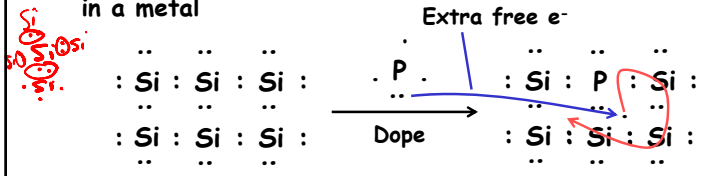





## Semiconductor Doping

## 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



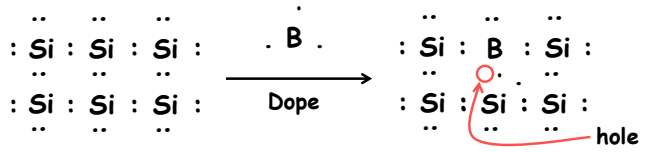
## Doping of Semiconductors (cont.)

- Conductivity Equation:

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

conductivity; electron mobility; electron density; charge magnitude on an electron; 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



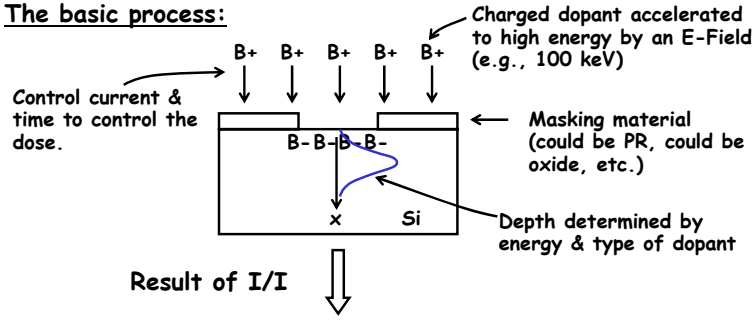
## Ion Implantation



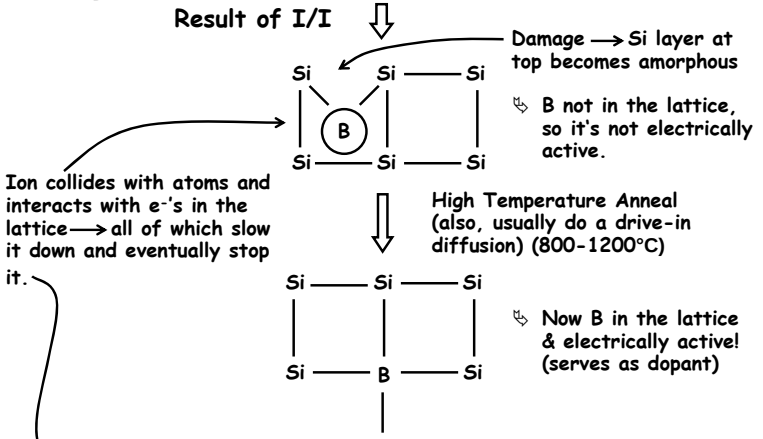
## Ion Implantation

- 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:

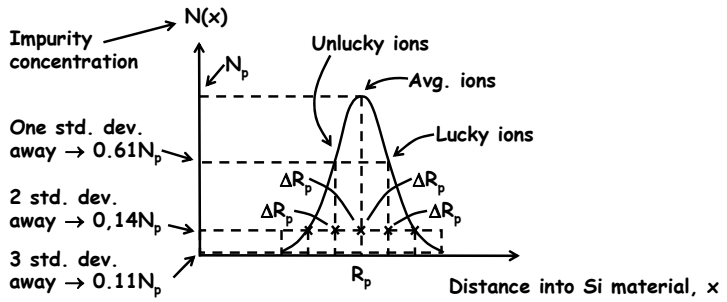


## Ion Implantation (cont.)






## 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.

$D_I = Q$

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



## I/I Range Graphs

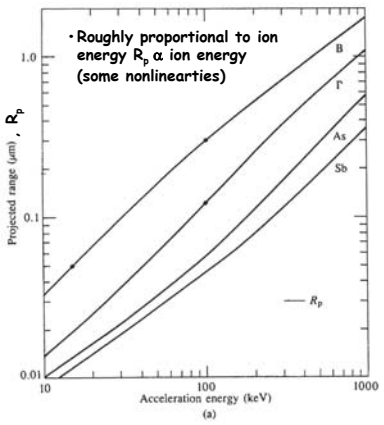



Figure 6.1

- $R_p$ is a function of the energy of the ion and atomic number of the ion and target material
- Lindhand, Scharff and Schiott (LSS) Theory:
- 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

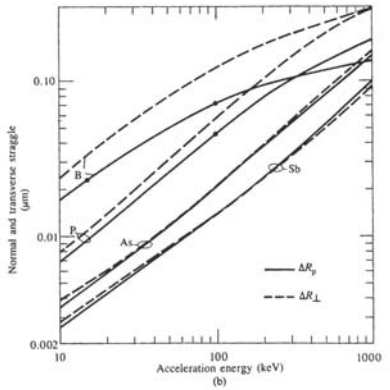



Figure 6.2

- Results for Si and $SiO_2$ surfaces are virtually identical → so we can use these curves for both

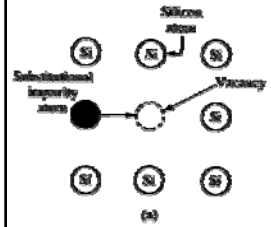


## Diffusion

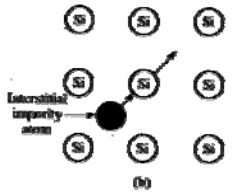


## Diffusion in Silicon

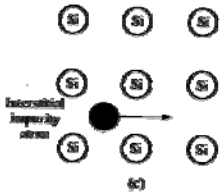
- Movement of dopants within the silicon at high temperatures
- Three mechanisms: (in Si)




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

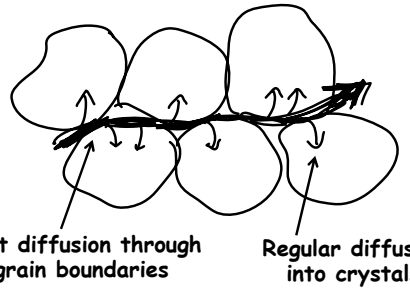



Interstitial Diffusion
- Impurity atoms jump from one interstitial site to another
- Get rapid diffusion
  - Hard to control
  - Impurity not in lattice so not electrically active



## 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

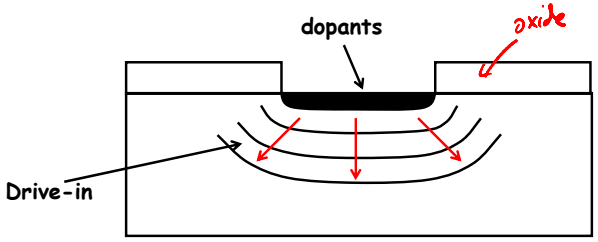



- In effect, larger surface area allows much faster volumetric diffusion

## 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 $N_2/O_2$

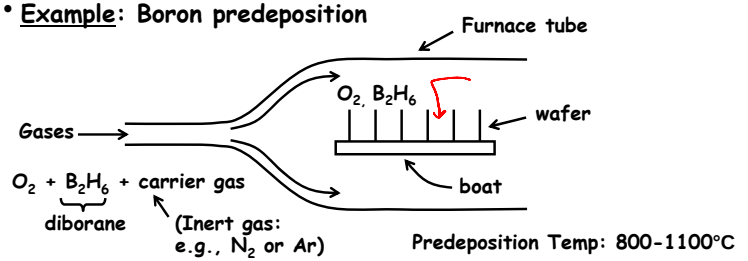
- Result:






## Predeposition

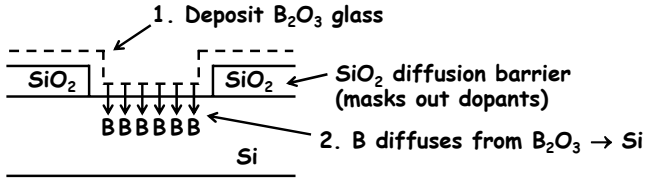
- Furnace-tube system using solid, liquid, or gaseous dopant sources
- Used to introduced a controlled amount of dopants
  - Unfortunately, not very well controlled
  - Dose (Q) range: $10^{13}$ – $10^{16}$ ± 20%
  - For ref: w/ ion implantation: $10^{11}$ – $10^{16}$ ± 1% (larger range & more accurate)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



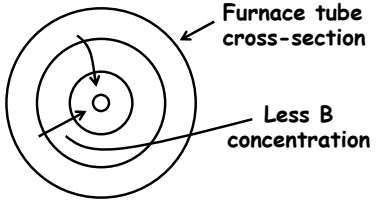



## Ex: Boron Predeposition

- Basic Procedure:



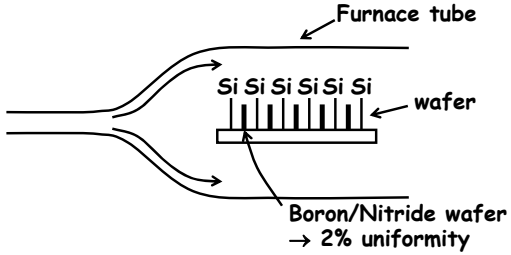

- Difficult to control dose Q, because it's heavily dependent on partial pressure of $B_2H_6$ gas flow
  - this is difficult to control itself
  - get only 10% uniformity






## Ex: Boron Predeposition (cont.)

For better uniformity, use solid source:




Reactions:

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

$Si + O_2 \rightarrow SiO_2$

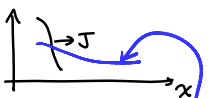
## General Comments on Predeposition

- 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

Modeling N(x)




⇒ 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)

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

J: flux [#/cm²·s]; D: 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



## Diffusion Modeling (cont.)

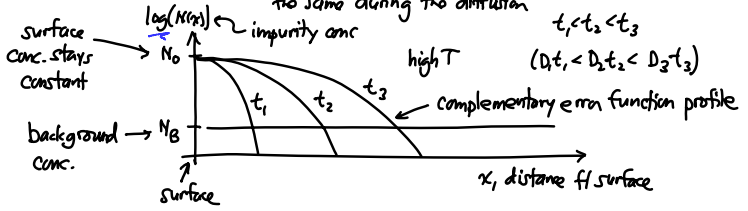
⇒ we're interested for now in the one-dimensional form:

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

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

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






## Diffusion Modeling (Predeposition)

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


⇒ Boundary Conditions:

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

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

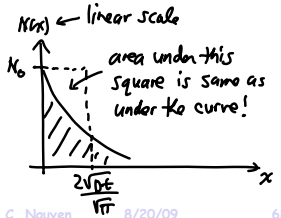
$$N(x,t) = N_0\,\mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

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

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

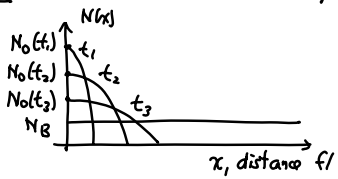
$$Q = \int_0^\infty N(x,t)dx \Rightarrow \boxed{Q(t) = N_0\frac{2\sqrt{Dt}}{\sqrt{\pi}}\ cm^{-2}}$$

$2\sqrt{Dt}$ ≜ characteristic diffusion length



## Diffusion Modeling (Limited Source)

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

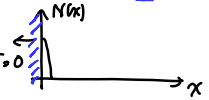



⇒ Boundary Condition:

(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! ↑ Assumption.






## Diffusion Modeling (Limited Source)

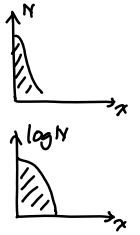
(iii) Usually make delta fcn. approx.: $N(x,0) = Q\,\delta(x)$

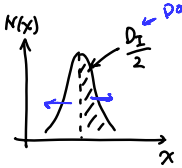
⇒ we can do this, because for sufficiently long diffusion times, no matter what the original shape of the dopant distribution, the diffused distribution will be the same

Get Gaussian Distribution:

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

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

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

in the Gaussian distribution expression.