Wet Etch Limitations (cont.)

7. Bubble formation (as a reaction by-product)
   - If bubbles cling to the surface → get nonuniform etching

   ![Diagram](image)
   - Bubble (gaseous by-product)
   - Non-uniform etching
   - Solution: Agitate wafers during reaction.

Some Common Wet Etch Chemistries

Wet Etching Silicon:

- **Common:** Si + HNO₃ + 6HF → H₂SiF₆ + HNO₂ + H₂ + H₂O
  - (isotropic)
  - (nitric acid)
  - (hydrofluoric acid)

  1. forms a layer of SiO₂
  2. etches away the SiO₂

  Different mixture combinations yield different etch rates.

Silicon Crystal Orientation

- **Orientation-dependent etching:** <111>-plane more densely packed than <100>-plane
- Faster E.R.
- Slower E.R.

Anisotropic Wet Etching

Anisotropic etches also available for single crystal Si:

- Orientation-dependent etching: <111>-plane more densely packed than <100>-plane
- One such solvent: KOH + isopropyl alcohol
  - (e.g., 23.4 wt% KOH, 13.3 wt% isopropyl alcohol, 63 wt% H₂O)

  \[ \text{E.R.}_{100} = 100 \times \text{E.R.}_{111} \]
Anisotropic Wet Etching (cont.)

Can get the following:

(on a <100> - wafer)

\[
\begin{align*}
\text{SiO}_2 & \quad \text{<111>} \\
\text{Si} & \quad \text{<100>} \\
\end{align*}
\]

54.7°

(on a <110> - wafer)

\[
\begin{align*}
\text{SiO}_2 & \quad \text{<111>} \\
\text{Si} & \quad \text{<110>} \\
\end{align*}
\]

Quite anisotropic!

Wet Etching SiO\textsubscript{2}

\[
\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2 + \text{SiF}_6 + 2\text{H}_2\text{O}
\]

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

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 lifts during such etching
  - Solution: use SiO\textsubscript{2} as an etch mask (E.R. ~2.5 nm/min)
    - A hassle to dry etch processes more common than wet
- Wet etching aluminum
  - Typical etch solution composition:
    - 80% phosphoric acid, 5% nitric acid, 5% acetic acid, 10% water
    - \((\text{H}_2\text{PO}_4)\) \((\text{HNO}_3)\) \((\text{CH}_3\text{COOH})\) \((\text{H}_2\text{O})\)
    - (1) Forms \(\text{Al}_2\text{O}_3\) (aluminum oxide)
    - (2) Dissolves the \(\text{Al}_2\text{O}_3\)
  - Problem: \(\text{H}_2\) gas bubbles adhere firmly to the surface → delay the etch → need a 10-50% overetch time
  - Solution: mechanical agitation, periodic removal of wafers from etching solution
**Film Etch Chemistries**

* For some popular films:

<table>
<thead>
<tr>
<th>Material</th>
<th>Wet etchant</th>
<th>Etch rate [nm/min]</th>
<th>Dry etchant</th>
<th>Etch rate [nm/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysilicon</td>
<td>HNO$_3$, H$_2$O: NH$_4$F</td>
<td>120-600</td>
<td>SF$_6$, He</td>
<td>170-920</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>H$_3$PO$_4$</td>
<td>5</td>
<td>SF$_6$</td>
<td>150-250</td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>HF</td>
<td>20-2000</td>
<td>CHF$_3$, O$_2$</td>
<td>50-150</td>
</tr>
<tr>
<td>Aluminum</td>
<td>H$_2$PO$_4$, HNO$_3$: CH$_3$COOH</td>
<td>680</td>
<td>Cl$_2$, SiCl$_4$</td>
<td>100-150</td>
</tr>
<tr>
<td>Photoresist</td>
<td>Acetone</td>
<td>&gt;4000</td>
<td>O$_2$</td>
<td>35-3500</td>
</tr>
<tr>
<td>Gold</td>
<td>KI</td>
<td>40</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

**Dry Etching**

- Physical sputtering
- Plasma etching
- Reactive ion etching

All based upon plasma processes.

- (+) ions generated by inelastic collisions with energetic e$^-$'

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

Develops (+) charge to compensate for

- High energy and directionality using E-fields
- Highly directional → very anisotropic

**Physical Sputtering (Ion Milling)**

- Bombard substrate w/ energetic ions → etching via physical momentum transfer
- Plasma (partially ionized gas composed of ions, e$^-$, and highly reactive neutral species)

Develops (+) charge to compensate for

- Steep vertical wall
**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.
6. Desorbed species diffuse into the bulk of the gas

**Ex: Polysilicon Etching w/ CF₄ and O₂**

\[ 	ext{CF}_4 \rightarrow \text{CF}_4^+ + \text{CF}_3^+ + \text{CF}_2^+ + \text{CF}^+ + F^+ + F^0 + \text{CF}_2^- + \ldots \]

Neutral radical (highly reactive!)

\[ \text{SiC}_6, \text{SiF}_4 \leftarrow \text{both volatile} \Rightarrow \text{dry etching is possible.} \]

* F° is the dominant reactant → but it can't be given a direction → thus, get isotropic etch!

**Ex: Polysilicon Etching w/ CF₄ and O₂**

- Isotropic etching
- Formation of polymer because of C in CF₄

* Solution: add O₂ to remove the polymer (but note that this reduces the selectivity, \( S_{\text{poly/PR}} \))

* 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

**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

**Deep Reactive-Ion Etching (DRIE)**

- Inductively-coupled plasma  
- Etch Rate: 1.5-4 μm/min  
- Two main cycles in the etch:  
  - Etch cycle (5-15 s): SF₆ (SFₓ⁺) etches Si  
  - Deposition cycle (5-15 s): C₄F₈ deposits fluorocarbon protective polymer (CF₂⁻)ₙ

- Etch mask selectivity:  
  - SiO₂ ~ 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

- 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
  - Extra free e⁻
    
    | Si | Si | Si | P | Si | P | Si |
    |----|----|----|---|----|---|----|
    | Si | Si | Si | Dope | Si | Si | Si |

- The larger the # of donor atoms, the larger the # of free e⁻’s → the higher the conductivity

Doping of Semiconductors (cont.)

- Conductivity Equation:
  \[
  \sigma = q \mu_n n + q \mu_p p
  \]

- If fewer e⁻’s, then the dopant is an acceptor: B
  
  | Si | Si | Si | B | Si | B | Si |
  
  | Si | Si | Si | Dope | Si | Si | Si |

- 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

Method by which dopants can be introduced into 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.)

Statistical Modeling of I/I

Result of I/I
- Damage → Si layer at top becomes amorphous
- B not in the lattice, so it’s not electrically active.
- Si → Si → Si
- High Temperature Anneal (also, usually do a drive-in diffusion) (800-1200°C)
- Now B in the lattice & electrically active (serves as dopant)
- Si → B → Si

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

Impurity concentration
- One std. dev. away → 0.61N_p
- 2 std. dev. away → 0.14N_p
- 3 std. dev. away → 0.11N_p

Distance into Si material, x

N(x)
- Unlucky ions
- Avg. ions
- Lucky ions

ΔR_p → Projected range = avg. distance on ion trends before stopping
ΔR_p → 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 = \[ Q = \int_{0}^{\infty} N(x) \, dx \quad \text{[ions/cm}^2\text{]} \]

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)

\[ D_I = \frac{Q}{\Delta R_p} \]

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

---

I/I Range Graphs

- \( R_p \) is a function of the energy of the ion and atomic number of the ion and target material
- Lindhard, 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

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

Fast diffusion through grain boundaries
Regular diffusion into crystals

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 $> 900^\circ\text{C}$ in $N_2$ or $N_2/O_2$
   - Result:

Predeposition

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

Gases
$O_2 + B_2H_6 + \text{carrier gas}$
(Inert gas: e.g., $N_2$ or $Ar$)

Diborane

Furnace tube

Boat

Predeposition Temp: $800-1100^\circ\text{C}$
Ex: Boron Predeposition

1. Deposit B₂O₃ glass
2. B diffuses from B₂O₃ → Si

Diffusion barrier (masks out dopants)

* Basic Procedure:

• Difficult to control dose Q, because it's heavily dependent on partial pressure of B₂H₆ gas flow
• this is difficult to control itself
• get only 10% uniformity

For better uniformity, use solid source:

Reactions:
B₂H₆ + 3O₂ → 3H₂O + B₂O₃
Si + O₂ → SiO₂

General Comments on Predeposition

• Higher doses only: Q = 10¹³ – 10¹⁶ cm⁻² (I/I is 10¹¹ – 10¹⁶)
• 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 ~10²⁰ 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

Fick’s law of diffusion - (1st law)

\[ J(x,t) = -D \frac{\partial N(x,t)}{\partial x} \]  

(1)

Continuity Equation for Particle Flux -
General Form

\[ \frac{\partial N(x,t)}{\partial t} + \nabla \cdot J = \frac{\partial (\rho n)}{\partial t} \] 

rate of increase of conc. in time


**Diffusion Modeling (cont.)**

We're interested in new in the one-dimensional form:

\[
\frac{\partial N(x,t)}{\partial t} = D \frac{\partial^2 N(x,t)}{\partial x^2} \quad \text{[Fick's 2nd Law of Diffusion in 1-D]}
\]

**Solution:**
- depends upon boundary conditions
- use variable separation or replace X transform technique

**Case 1:** Deposition, constant source diffusion: surface concentration stays the same during the diffusion.

\[
\begin{align*}
\text{surface conc.:} & \quad N_s \\
\text{conc.:} & \quad N_b
\end{align*}
\]

**Diffusion Modeling (Predeposition)**

If plotted on a linear scale, would look like this:

\[
N(x,t) \approx \begin{cases} 
N_0 & t > \frac{2b^2}{D} \\
N_b & t < \frac{2b^2}{D}
\end{cases}
\]

**Boundary Conditions:**
- \( N(x,t) = N_0 \) when \( x = 0 \)
- \( N(x,t) = 0 \) when \( x = b \)

\[
N(x,t) = N_0 \cosh \left( \frac{x}{2b} \right)
\]

where \( \cosh \) is the hyperbolic cosine function (read table or graph)

Dose, \( Q \) is total # of impurity atoms per unit area in the Si.

\[
Q = \int_0^b N_s(x)dx \approx Q(b) = \frac{2bQ_0}{\sqrt{\pi}} \quad \text{cm}^{-2}
\]

[2b \sqrt{\pi} = characteristic diffusion length]

**Diffusion Modeling (Limited Source)**

**Case 2:** Drive-in, limited source diffusion, i.e., constant dose \( Q \)

\[
\begin{align*}
N_0(x) & = \text{initial concentration} \\
N_b(x) & = \text{boundary concentration} \\
N_s(x) & = \text{source concentration}
\end{align*}
\]

**Boundary Conditions:**
- \( N_0(x,t) = N_b \) for \( x = b \)
- \( \frac{\partial N(x,t)}{\partial x} = Q - \text{const.} \) for \( x = 0 \)

This is equivalent to saying that there's no flux going out of the Si, i.e., \( \phi = 0 \).

\[ \int_0^b \frac{\partial N(x,t)}{\partial x} dx = \text{constant} \]

When the starting concentration profile is completely contained in the Si, then

\[
Q \cdot \frac{b^2}{8} = \text{half the implant dose}
\]
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:
  \[(D_t)_{\text{predep}} \gg (D_t)_{\text{drive-in}} \Rightarrow \text{impurity profile is complementary error function}\]
  \[(D_t)_{\text{drive-in}} \gg (D_t)_{\text{predep}} \Rightarrow \text{impurity profile is Gaussian (which is usually the case)}\]

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 \((D_t)_1 = (\Delta R_p)^2/2\) (Gaussian)
     - Drive-in/activation → \(D_2 t_2\)
  2. Other high temperature steps
     - (e.g., oxidation, reflow, deposition) → \(D_3 t_3\), \(D_4 t_4\), ...
     - Each has their own Dt product
  3. Then, to find the final profile, use
  \[(D_t)_{\text{tot}} = \sum_i D_i t_i\]
  in the Gaussian distribution expression.

The Diffusion Coefficient

\[D = D_o \exp\left(-\frac{E_A}{kT}\right)\] (as usual, an Arrhenius relationship)

<table>
<thead>
<tr>
<th>Element</th>
<th>(D_o (\text{cm}^2/\text{sec}))</th>
<th>(E_A (\text{eV}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>10.5</td>
<td>3.69</td>
</tr>
<tr>
<td>Al</td>
<td>8.00</td>
<td>3.47</td>
</tr>
<tr>
<td>Ga</td>
<td>3.60</td>
<td>3.51</td>
</tr>
<tr>
<td>In</td>
<td>16.5</td>
<td>3.90</td>
</tr>
<tr>
<td>P</td>
<td>10.5</td>
<td>3.69</td>
</tr>
<tr>
<td>As</td>
<td>0.32</td>
<td>3.56</td>
</tr>
<tr>
<td>Sb</td>
<td>5.60</td>
<td>3.95</td>
</tr>
</tbody>
</table>

Diffusion Coefficient Graphs

- Interstitial Diffusers
  - Note the much higher diffusion coefficients than for substitutional

Substitutional & Interstitial Diffusers

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Metallurgical Junction Depth, $x_j$

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

Log[$N(x)$] - Net impurity conc.

Log[$N(x) - N_B$] - e.g., p-type Gaussian

$p$-type region

Log[$N(x)$] - e.g., n-type Gaussian

$n$-type region

$x = \text{distance from surface}$

Expressions for $x_j$

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

$$N(x_j, t) = N_o \exp \left( -\left( \frac{x_j}{2\sqrt{D}t} \right)^2 \right) = N_B \quad \Rightarrow \quad x_j = 2\sqrt{D}t \ln \left( \frac{N_o}{N_B} \right)$$

* For a complementary error function profile:

$$N(x_j, t) = N_o \text{erfc} \left( \frac{x_j}{2\sqrt{D}t} \right) = N_B \quad \Rightarrow \quad x_j = 2\sqrt{D}t \text{erfc}^{-1} \left( \frac{N_B}{N_o} \right)$$

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:

$$R = \frac{\rho L}{A} + \frac{\rho x}{W} = \frac{\rho L}{A} + \frac{\rho x}{W}$$

- $\rho$: sheet resistance

- $L$: length of material

- $W$: width of material

$$\sigma = \text{conductivity} = q\mu_n + q\mu_p$$

- $q$: charge of electron

- $\mu_n$: electron mobility

- $\mu_p$: hole mobility

- $R = R_s \times S$

* 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:
  \[ R_s = \frac{\rho}{x_j} = \left[ \int_0^{x_j} \sigma(x) \, dx \right]^{-1} = \left[ \int_0^{x_j} q\mu N(x) \, dx \right]^{-1} \]
  
  [extrinsic material]

- This expression neglects depletion of carriers near the junction, \( x_j \to \) 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 \( x_j \), \( N_s \) (the surface concentration), and \( N_B \) (the substrate background conc.)

Irvin's Curves (for n-type diffusion)

Example. Given:
  \( N_B = 3 \times 10^{16} \, \text{cm}^{-3} \)
  \( N_s = 1.1 \times 10^{18} \, \text{cm}^{-3} \)
(p-type Gaussian)
  \( x_j = 2.77 \, \mu m \)

Can determine these given known predep. and drive conditions

Determine the \( R_s \):

Using Fig. 7.7:
  \( R_s x_j = 4.7 \frac{\Omega}{\mu m} \)

\( R_s = \frac{4.7}{2.77} \approx 17 \, \Omega / \mu m \)