Text Book:
Silicon VLSI Technology
Fundamentals, Practice and Modeling
Authors: J. D. Plummer, M. D. Deal, and P. B. Griffin
• Etching of thin films and sometimes the silicon substrate are very common process steps.
• Usually selectivity, and directionality are the first order issues.
• Selectivity comes from chemistry; directionality usually comes from physical processes. Modern etching techniques try to optimize both.
• Simulation tools are beginning to play an important role in etching just as they are in deposition. Topography simulators often do both, based on the same physical principles.
Etch Profiles

Illustration of (a) undercutting (directionality) and (b) selectivity issues.

- Usually highly anisotropic (almost vertical profiles) and highly selective etching (ratios of 25-50) are desired, but these can be difficult to achieve simultaneously.

General etch requirements:

1. Obtain desired profile (sloped or vertical)
2. Minimal undercutting or bias
3. Selectivity to other exposed films and resist
4. Uniform and reproducible
5. Minimal damage to surface and circuit
6. Clean, economical, and safe
Historical Development and Basic Concepts

- There are two main types of etching used in IC fabrication: wet etching and dry or plasma etching. Plasma etching dominates today.

**Wet Etching and General Etching Ideas**

- Processes tend to be highly selective but isotropic (except for crystallographically dependent etches).

Examples:

   Etching of SiO$_2$ by aqueous HF:
   
   (1) \( \text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \)

   Etching of Si by nitric acid (HNO$_3$) and HF:
   
   (2) \( \text{Si} + \text{HNO}_3 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + \text{HNO}_2 + \text{H}_2\text{O} + \text{H}_2 \)

- Wafers typically submerged in specific chemical baths and rinsed in DI H$_2$O.
Isotropic Etching: Typical of Wet Etching

- Isotropic etching implies undercutting. This is often expressed in terms of the etch bias $b$.
- Etch anisotropy is defined as:
  \[ A_f = 1 - \frac{r_{lat}}{r_{ver}} = 1 - \frac{b}{d} \quad (3) \]
- $A_f = 0$ for isotropic etching since $r_{lat} = r_{ver}$.

- Some overetching, shown above at right, is usually done to ensure complete etching (due to variations in film thickness and etch rate).

- Selectivity is usually excellent in wet etching ($S = r_f/r_2$) since chemical reactions are very selective.
Wet Etching Selectivity

Example p. 613

- 1 um of SiO2 to be etched in a Si substrate.
- SiO2 etch rate: 0.40 um/min
- Selectivity with respect to SiO2:silicon is 25:1
- A three minute etch is performed:
  - 1 um SiO2 should take 2.5 min.
  - Si etch for 0.5 min at a rate of 0.40/25 = 0.016 um/min
  - Therefore, Si etch of 0.008 um or 8 nm

- HF or buffered HF etch of SiO2 has been common with the Si etch rate considered negligible.
  - Overetching commonly done due to high selectivity
Mask Erosion

- Mask erosion can be an issue for both isotropic and anisotropic etching profiles.

- Because of their isotropic nature, wet chemical etches are rarely used in mainstream IC manufacturing today, plasma etching is preferred.
Maintaining Device Dimensions

Example where equal structure width are desired:

Let \( A_f = 0.8 \) anisotropy, \( d = x_f = 0.5 \text{ um} \), \( x = 0.35 \text{ um} \)

Find \( S_m \) and \( S_f \)

\[
A_f = 1 - \frac{r_{wl}}{r_{wr}} = 1 - \frac{b}{d}
\]

\[
S_m + x = S_f + 2 \times b + x
\]

\[
S_m = S_f + 2 \times x_f \times (1 - A_f)
\]

\[
S_m = S_f + 2 \times x_f \times (1 - A_f)
\]

\[
2 \times S_f = S_m + x
\]

\[
2 \times S_f = S_f + 2 \times x_f \times (1 - A_f) + x
\]

\[
S_f = 2 \times x_f \times (1 - A_f) + x
\]

\[
S_f = 2 \times 0.5 \times (1 - 0.8) + 0.35 \text{ um}
\]

\[
S_f = 0.2 \text{ um} + 0.35 \text{ um}
\]

\[
S_f = 0.55 \text{ um}
\]

\[
S_m = 0.55 \text{ um} + 0.20 \text{ um}
\]

\[
S_m = 0.75 \text{ um}
\]
# Wet Etching – Isotropic Etch

<table>
<thead>
<tr>
<th>Material</th>
<th>Etchant</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>HF (49% in water)</td>
<td>Selective over Si (i.e., will etch Si very slowly in comparison). Etch rate depends on film density, doping. About 1/20 th the etch rate of straight HF. Etch rate depends on film density, doping. Will not lift up photoresist like straight HF.</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>HF (49%)</td>
<td>Each rate depends strongly on film density, O, H in film. Selective over SiO₂. Requires oxide mask.</td>
</tr>
<tr>
<td>Al</td>
<td>H₃PO₄·H₂O</td>
<td>Each rate depends on etchant composition. Selective over Si, SiO₂, and photoresist.</td>
</tr>
<tr>
<td>Polysilicon</td>
<td>HNO₃·H₂O·HF (+ CH₃·COOH) (50:2:1:1)</td>
<td>Each rate depends on etchant composition.</td>
</tr>
<tr>
<td>Single crystal Si</td>
<td>HNO₃·H₂O·HF (+ CH₃·COOH) (50:2:1)</td>
<td>Crystallographically selective; relative etch rates: (100): (100) (111):1</td>
</tr>
<tr>
<td>Photoresist</td>
<td>H₂SO₄·H₂O·IPA (23 wt. % KOH, 13 wt. % IPA)</td>
<td>For wafers without metal. For wafers with metal.</td>
</tr>
</tbody>
</table>
Plasma Etching

Developed and used for:
1. Faster and simpler etching in a few cases.
2. More directional (anisotropic) etching!!

- Typical RF-powered plasma etch system look just like PECVD or sputtering systems.
- Both chemical (highly reactive) species and ionic (very directional) species typically play a role.
- $V_p$ is positive to equalize electron and ion fluxes.
- Smaller electrode has higher fields to maintain current continuity (higher RF current density).
Plasma Reactions

- Typical reactions and species present in a plasma used are shown in the figure and below.

- Etching gases include halide-containing species such as CF₄, SiF₆, Cl₂, and HBr, plus additives such as O₂, H₂ and Ar. O₂ by itself is used to etch photoresist. Pressure = 1 mtorr to 1 torr.

- Typically there are about 10¹⁵ cm⁻³ neutral species (1 to 10% of which may be free radicals) and 10⁸-10¹² cm⁻³ ions and electrons.

- In standard plasma systems, the plasma density is closely coupled to the ion energy (as determined by the sheath voltage). Increasing the power increases both.
Plasma Etching Mechanisms

- There are three principal mechanisms based on the reactive neutral species and the ions:
  - chemical etching (isotropic, selective)
  - physical etching (anisotropic, less selective)
  - ion-enhanced etching (anisotropic, selective)

- Reactive Neutrals: Form free radicals that are primarily responsible for chemical component of the etch process.
- Ions: Physical component of etch or sputtering.
Chemical Etching

- Etching done by reactive neutral species, such as “free radicals” (e.g. F, CF₃)
  \[ e^- + CF_3 \rightarrow CF_3 + F + e^- \]  
  \[ 4F + Si \rightarrow SiF_4 \]

- Additives like O₂ can be used which react with CF₃ and reduce CF₃ + F recombination. \( \therefore \) higher etch rate.
- These processes are purely chemical and are therefore isotropic and selective, like wet etching.
- Generally characterized by \( \cos^n \theta \) (n=1) arrival angle and low sticking coefficient \( S_e \approx 0.01 \).
Physical Etching

- Ion etching is much more directional (E field across plasma sheath) and $S_c \approx 1$, i.e. ions don't bounce around (or if they do, they lose their energy.)

- Etching species are ions like $\text{Cl}^+$, $\text{CF}_3^+$ or $\text{Ar}^+$ which remove material by sputtering.

- Not very selective since all materials sputter at about the same rate.

- Physical sputtering can cause damage to surface, with extent and amount of damage a direct function of ion energy (not ion density).

Rate based on the sputter yield discussed in Chap. 9
Ion Enhanced Etching

- The chemical and physical components of plasma etching do not always act independently - both in terms of net etch rate and in resulting etch profile.

- Figure shows etch rate of silicon as XeF₂ gas (not plasma) and Ar⁺ ions are introduced to the silicon surface. Only when both are present does appreciable etching occur.

- Etch profiles can be very anisotropic, and selectivity can be good.

- Many different mechanisms proposed for this synergistic etching between physical and chemical components.
Ion Enhanced Etching

- Ion bombardment can (a) enhance etch process (such as by damaging the surface to increase reaction, or by removing etch byproducts), or can (b) remove inhibitor that is an indirect byproduct of etch process (such as polymer formation from carbon in gas or from photoresist).

- Whatever the exact mechanism (multiple mechanisms may occur at same time):
  - Need both components for etching to occur.
  - Get anisotropic etching and little undercutting because of directed ion flux.
  - Get selectivity due to chemical component and chemical reactions.

Therefore, many applications in etching today.
Ion-Enhanced Etch Inhibitor Effects

- Can actually get sloped sidewalls without undercutting.
- Depends on ratio of inhibitor formation ("deposition") to etching, as shown.
  (a) faster deposition
  (b) slower deposition
Types of Plasma Etching Systems

- Different configurations have been developed to make use of chemical, physical or ion assisted etching mechanisms
- Barrel Etchers
- Parallel Plate Systems - Plasma Mode
- Parallel Plate Systems - Reactive (and) Ion Etching (RIE) Mode
- High Density Plasma (HDP) Etch Systems
- Sputter Etching
Barrel Etchers

- Purely chemical etching. No ionic bombardment.
  - Isotropic, poor uniformity from outside edge to inside wafers

- Used for non-critical steps, such as photoresist removal (ashing).
  - Uses an O₂ plasma
Parallel Plate Systems - Plasma Mode

• Electrodes have equal areas (or wafer electrode is grounded with chamber and therefore larger)
• Strong chemical component.
• Only moderate sheath voltage (10-100 eV), so only moderate ionic component.
• Etching can be fairly isotropic and selective. Used for films.
Parallel Plate Systems - Reactive (and) Ion Etching (RIE)

- Same structure as before modified to enhance physical (ion) component
  - For more directed etching, need stronger ion bombardment.

- Wafers sit on smaller electrode (RF power there).

- Higher voltage drop across sheath at wafers. (100-700 eV).

- Lower pressures are used to attain even more directional etching (10-100 mtorr).

- More physical component than plasma mode; therefore, directionality but less selectivity.
High Density Plasma (HDP) Etch Systems

- Uses remote, non-capacitively coupled plasma source (Electron cyclotron resonance - ECR, or inductively coupled plasma source - ICP).

- Uses separate RF source as wafer bias. This separates the plasma power (density), from the wafer bias (ion accelerating field).

- Very high density plasmas ($10^{11} - 10^{12}$ ion cm$^{-3}$) can be achieved (faster etching).

- Lower pressures (1-10 mtorr range) can be utilized due to higher ionization efficiency (a longer mean free path and more anisotropic etching).

- These systems produce high etch rates, decent selectivity, and good directionality, while keeping ion energy and damage low. Therefore, widely used.
Sputter Etching

- **Purely physical etching:**
  - Highly directional, with poor selectivity
  - Can etch almost anything
- **Sputter etching, uses Ar+:**
  - Damage to wafer surface and devices can occur: trenching (a), ion bombardment damage, radiation damage, redeposition of photoresist (b) and charging and ion path distortion (c).
- **These can occur in any etch system where the physical component is strong.**
Plasma Etching Summary (1)

Pressure

Energy

Selectivity

Anisotropy

Sputter Etching and Ion Beam Milling

High Density Plasma Etching

Reactive Ion Etching

Plasma Etching

Wet Chemical Etching

Physical Processes

Chemical Processes
Plasma Etching Summary (2)

- **Physical**
  - Ionic species
  - Mask erosion, inlet gases
  - Removed on horizontal surfaces by ion bombardment
  - A possible mechanism in ion enhanced etching

- **Chemical**
  - Reactive neutral species
  - Free radicals important

- **Charging**
  - Mask erosion

- **Undercutting**
  - Chemical etching
    - Isotropic, very selective

- **Sidewall-inhibitor Deposition**
  - Sources: etch byproducts, mask erosion, inlet gases
  - Removed on horizontal surfaces by ion bombardment
  - A possible mechanism in ion enhanced etching

- **Physical etching**
  - Anisotropic, non-selective

- **Ion Enhanced Etching**
  - Needs both ions and reactive neutrals
  - May be due to enhanced etch reaction or removal of etch byproduct or inhibitor
  - Anisotropic, selective
Manufacturing Methods

- **Conditions and Issues**
  - Gas composition and flow rates – controlled to find desired characteristics
  - Temperature – control and minimize the temperature rise on the wafer surface (wafer cooling)
  - Selectivity – chemical reactants in proper proportions
  - Etch profile control – typically vertical or near-vertical desired, chemistry to favor physical etch or form inhibitor.
  - Etch uniformity – bulls-eye depletion effects from wafer outside edge to center
  - “Loading Effects”
    - Macroscopic – more wafers with more etch area result in slower etch rates due to depletion of etchant
    - Microloading – etch rates vary over small distances (based on aspect ratios)
Gas Composition - Influence on Selectivity

Figure 10-21: Etch rate of polysilicon and photoresist, and resulting taper angle as a function of C₂H₆ in Cl₂/C₂H₆ etch chemistry. More C₂H₆ results in more sidewall inhibitor formation and deposition relative to etching. (After [10.8].)

Sidewalls affected by the polymer formation

Stronger deposition of polymer
Gas Composition - Influence on Selectivity

H₂ increase effects SiO₂/Si selectivity in CF₄ and decreases PR erosion
Aspect Ratio Dependent Etching

- Two kinds of loading problems
  - Macroloading – etch rate varies over due to number of wafers or large regions to be etched. General depletion of etchant
  - Microloading – dependence of etch rate on feature size, aspect ratio. Depletion and distortion of ion path: depletion or trapping, charging of wafer may distort path, shadowing
Film Thickness: Over Etching may be required

Stringers must be removed unless they act as spacers.

Gas is selected to ensure selectivity and high volatility of byproducts.

Figure 10-33 Overetching of a film over a step would be required to remove material at corner. In this example, completely anisotropic etching is assumed to emphasize this concept. This phenomenon can be used in producing self-aligned oxide spacers, in which no extra overetching is done so as to intentionally produce the structure at the right.
Inhibitor Deposition Effects

(a) Little or No Inhibitor Deposition (e.g. CF$_4$ + O$_2$)
(b) Inhibitor Deposition (e.g. CF$_4$ + H$_2$ or CHF$_3$ + O$_2$) - increased C/F
(c) Excess Inhibitor Deposition (e.g. CHF$_3$)

OXIDE ETCHING: (4F + SiO$_2$ → SiF$_4$ + O$_2$)
(a) CF$_4$ + O$_2$
(b) CF$_4$ + H$_2$ or CHF$_3$ + O$_2$ - increased C/F
(c) CHF$_3$ - increased C/F

- C/F causes an increase in polymer formation
- Increased O$_2$ causes a decrease in C and decrease polymer formation
- Increased O$_2$ causes an increase in PR etch leading to mask erosion
Plasma Etching for Various Films

<table>
<thead>
<tr>
<th>Material</th>
<th>Etchant</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysilicon</td>
<td>SF₆, CF₄</td>
<td>Isotropic or near isotropic (significant undercutting); poor or no selectivity over SiO₂</td>
</tr>
<tr>
<td></td>
<td>CF₄/H₂, CHF₃</td>
<td>Very anisotropic; nonselective over SiO₂</td>
</tr>
<tr>
<td></td>
<td>CF₄/O₂</td>
<td>Isotropic or near isotropic; more selective over SiO₂</td>
</tr>
<tr>
<td></td>
<td>HBr, Cl₂, Cl₂/HBr/O₂</td>
<td>Very anisotropic; most selective over SiO₂</td>
</tr>
<tr>
<td>Single-crystal Si</td>
<td>same etchants as polysilicon</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>SF₂, NF₃, CF₄/O₂, CO₂</td>
<td>Can be near isotropic (significant undercutting); anisotropy can be improved with higher ion energy and lower pressure; poor or no selectivity over Si.</td>
</tr>
<tr>
<td></td>
<td>CF₄/H₂, CHF₃/O₂, CF₆, C₄F₆</td>
<td>Very anisotropic; selective over Si.</td>
</tr>
<tr>
<td></td>
<td>CHF₃/C₄F₆/CO</td>
<td>Anisotropic; selective over SiNₓ.</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>CF₄/O₂</td>
<td>Isotropic; selective over SiO₂ but not over Si.</td>
</tr>
<tr>
<td></td>
<td>CF₄/CH₃</td>
<td>Very anisotropic; selective over Si but not over SiO₂</td>
</tr>
<tr>
<td>Al</td>
<td>Cl₂, Cl₂/CHCl₃, Cl₂/N₂</td>
<td>Very anisotropic; BCl₃ often added to scavenging oxygen.</td>
</tr>
<tr>
<td>W</td>
<td>CF₄, SF₆, Cl₂</td>
<td>High etch rate; nonselective over SiO₂.</td>
</tr>
<tr>
<td>Ti</td>
<td>Cl₂, Cl₂/CHCl₃, CF₄</td>
<td>Selective over SiO₂.</td>
</tr>
<tr>
<td>TiN</td>
<td>Cl₂, Cl₂/CHCl₃, CF₄</td>
<td></td>
</tr>
<tr>
<td>TiSi₂</td>
<td>Cl₂, Cl₂/CHCl₃, CF₄/O₂</td>
<td></td>
</tr>
<tr>
<td>Phototherm</td>
<td>O₂</td>
<td>Very selective over other films.</td>
</tr>
</tbody>
</table>
In Situ Measurement Method

• Optical Emission Spectroscopy
  – In a plasma, light (photons) is emitted by excited atoms and molecules as electrons relax from one energy level to a lower energy state.
    • The photons emitted have a wavelength indicative of the change in energy level.
    • Energy gaps are sufficiently distinct to determine the atom/molecule type that emitted them.
    • Changes in the number of photons emitted are indicative of the etch process … proceeding or completed.
  – Monitor free radical concentration.
    • Decreased while etch is in progress, rises when done
  – Monitor etchant product
    • At a specific level while etch is in progress, drops when etch is completed.
Models and Simulation

- There is a great deal of similarity between the deposition models described in Chapter 9 and etching models.
- Both use incoming "chemical" (neutral) and ion fluxes and many other similar physical processes.
- As in deposition, the etch rate is proportional to the net flux arriving at each point.
Models and Simulation

\[ F_{\text{direct}}(\theta) = F^* \cos^n \theta \]

- Chemical etching species are assumed to arrive isotropically \((n = 1 \text{ in } \cos^n \theta)\).

- Ionic species are assumed to arrive anisotropically (vertically) \((n \approx 10 - 80 \text{ in } \cos^n \theta)\).

- The "sticking coefficient" concept is used as in the deposition case. Ionic species usually "stick" \((S_c = 1)\), while reactive neutral species have low \(S_c\) values (bounce around).

- Sputtering yield has same angle dependence used in the deposition case.
Linear Etch Model

- While machine specific models have been developed, we will consider here general purpose etch models which can be broadly applied.

- Linear etch model assumes chemical and physical components act independently of each other (or appear to act independently for a range of conditions).

- 
  \[ \text{Eth rate} = \frac{S_i K_i F_c + K_i F_i}{N} \]  

- \( F_c \) and \( F_i \) are the chemical flux and ionic flux respectively, which will have different incoming angular distributions and vary from point to point.

- \( K_i \) and \( K_f \) are relative rate constants for two components.

- Physical component (2nd term) can be purely physical sputtering, or can be ion-enhanced mechanism in regime where chemical flux not limiting ion etching.
SPEEDIE Simulation

\[ Etch \text{ rate} = \frac{(S_c K_f F_c + K_i F_i)}{N} \]

a). all chemical etching (ion flux=0);
b). All physical or ionic etching (chem flux=0);
c). half chemical, half physical.
Note: lateral etch rate under masking layer must be composed of chem flux only in this model

No photoresist etching assumed. (see Fig 10-28 in text)
Etching Uniformity: Aspect Ratio Dependent Etching (ARDE)

- Two kinds of loading problems
  - Macrolading – etch rate varies over due to number of wafers or large regions to be etched. General depletion of etchant
  - Microlading – dependence of etch rate on feature size, aspect ratio. Depletion and distortion of ion path: depletion or trapping, charging of wafer may distort path, shadowing.
Saturation - Adsorption Etch Model

- Used for ion-enhanced etching, when chemical (neutral) and physical (ion) etch components are coupled.
- Examples - the ion flux is needed to remove a byproduct layer formed by the chemical etching, or ion bombardment damage induces chemical etching.

\[
Etch \, Rate = \frac{1}{N} \cdot \frac{1}{\left( \frac{1}{K_c F_i} + \frac{1}{S_c F_c} \right)} \tag{8}
\]

- If either flux is zero, the overall etch rate is zero since both are required to etch the material.
- Etch rate saturates when one component gets too large relative to the other (limited by slower of two series processes).
- General approach with broad applicability. (But does not account for independently formed inhibitor layer mechanism, and does not model excess inhibitor formation.)
Saturation - Adsorption Etch Model Sim

- SPEEDIE simulation with saturation/absorption etch model (Figure 10-31 equal chemical and ion components):

- Note the anisotropic etching. Both chemical and ion flux is required with ion flux arriving with a vertical direction ($n$ is large in $\cos \theta$).

- Contours represent 30 seconds in the 240 second etch simulation.
Other Etching Simulations

- Avanti's TAUROUS-TOPOGRAPHY simulation using their dry etch model with simultaneous polymer deposition.

- Etching SiO$_2$ (over Si, with a photoresist mask)
  a) after 0.9 minutes
  b) after 1.8 minutes.

- This explicitly models inhibitor deposition and sputtering.

- One can see the sloped etch profile, without etch bias, due to the excess polymer deposition.
Summary of Key Ideas

- Etching of thin films is a key technology in modern IC manufacturing.
- Photoresist is generally used as a mask, but sometimes other thin films also act as masks.
- Selectivity and directionality (anisotropy) are the two most important issues.
  - Usually good selectivity and vertical profiles (highly anisotropic) are desirable.
  - Other related issues include mask erosion, etch bias (undercutting), etch uniformity, residue removal and damage to underlying structures.
- Dry etching is used almost exclusively today because of the control, flexibility, reproducibility and anisotropy that it provides.
- Reactive neutral species (e.g. free radicals) and ionic species play roles in etching.
  - Generally neutral species produce isotropic etching and ionic species produce anisotropic etching.
- Physical mechanisms:
  - Chemical etching involving the neutral species.
  - Physical etching involving the ionic species.
  - Ion-enhanced etching involving both species acting synergistically.
- Simulation tools are fairly advanced today and include models for chemical, physical and ion-enhanced etching processes.
- Incoming angular distributions of etching species and parameters like sticking coefficients are used to model etching (similar to deposition modeling).
ECE 541/ME 541
Microelectronic Fabrication Techniques

MW 4:00-5:15 pm

Etching

Zheng Yang
Major Fabrication Steps in MOS Process Flow

Used with permission from Advanced Micro Devices
Etching

Transformation of material into volatile state.

Oxidation: Transformation into Oxide
Nitridation: Transformation into Nitride
Ion-Implantation: Transformation into material with altered conducting properties
Etching Methods
Over/Underetching

A precise knowledge of the etching rate is necessary in order to prevent over/under-etching.
Basic etching languages

1. Etching type:
   • Dry etching
   • Wet etching

2. Etching rate:
   • Diffusion limited: reactant/product controlled, very sensitive to agitation
   • Activation limited: Surface reaction limited, very sensitive to temperature

\[
rate = R_0 \exp\left(-\frac{E_A}{KT}\right)
\]

- \( R_0 \) = rate constant (depends on reactant density)
- \( E_A \) = activation energy (in eV)
- \( T \) = Temperature (Kelvin)
- \( K \) = Boltzman's constant

3. Etching selectivity: etching rate difference between two materials

4. Etching outcome:
   • Isotropic
   • Anisotropic
Isotropic/Anisotropic

Anisotropic etching is directed. It can produce better defined features, less undercutting.
Selectivity

Etching rate depending on material to be etched:

Wet etching has good selectivity, i.e. approx. 1:30

Bad selectivity (i.e. 1:3) causes attack of the underlayer.
Isotropic and anisotropic etching

(a) Si

(b) Si

Isotropic: Etching rate is the same in all directions: This causes undercutting, i.e., materials removed under mask

Anisotropic: Etching rate is not the same in all directions

Example: Si (100) wafers have gone through wet etching with two different wet etchants, respectively. The results are shown here. What etching types are they?
Wet etching

![Diagram of wet etching process]

### Table 6-1 Properties of common chemical reagents

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molecular weight</th>
<th>Concentration†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrofluoric acid</td>
<td>HF</td>
<td>20.0</td>
<td>49%</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>63.0</td>
<td>69.5%</td>
</tr>
<tr>
<td>Acetic acid, &quot;Glacial&quot;</td>
<td>CH₃CO₂</td>
<td>60.0</td>
<td>99%</td>
</tr>
<tr>
<td></td>
<td>CH₃COOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>98.1</td>
<td>98%</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>98.0</td>
<td>85%</td>
</tr>
<tr>
<td>Ammonium fluoride</td>
<td>NH₄F</td>
<td>37.0</td>
<td>40%</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>NH₄OH</td>
<td>35.05</td>
<td>29%</td>
</tr>
</tbody>
</table>

† Concentration by weight, in water, as commonly supplied.
### Typical wet etchants

<table>
<thead>
<tr>
<th>COMMON ETCHANT</th>
<th>ETCH TEMP</th>
<th>RATE A/MIN</th>
<th>METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>HF &amp; NH$_4$F (1 : 8)</td>
<td>Room</td>
<td>700</td>
</tr>
<tr>
<td>SiO$_2$ (Vapox)</td>
<td>Acetic Acid &amp; NH$_4$F(2 : 1)</td>
<td>Room</td>
<td>1000</td>
</tr>
<tr>
<td>Aluminum</td>
<td>H$_3$PO$_4$ : 16</td>
<td>40 - 50°C</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>HNO$_3$ : 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetic : 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_2$O : 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wetting Agent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>H$_3$PO$_4$</td>
<td>150 - 180°C</td>
<td>80</td>
</tr>
<tr>
<td>POLYSi</td>
<td>HNO$_3$ : 50</td>
<td>Room</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>H$_2$O : 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HF : 3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Wet etching methods

Immersion

Spray

Etchant

DI Water Rinse
**Silicon Wet Etch**

Active Ingredients:
HF, HNO$_3$

Solvent: Water

The etching reaction is exothermic. Control of temperature necessary. Acetic acid might be used for further control of etch rate

Si(100)  Si(111)
SiO$_2$ etching

- Can be used as gate oxide of a MOSFET
- Can be used as mask for ion implantation or diffusion
- Can be used as insulator between conductors
- Grown by furnace oxidation (wet/dry)
- Can also be formed by chemical vapor deposition
- Etched with HF solutions:

$$SiO_2 + 6 \text{HF} \rightarrow H_2 + SiF_6 + 2 H_2O$$

- Full-strength HF has high etching rate of 300Å/s at RT for SiO$_2$, for better process control, buffered oxide etch (BOE) with a mixture of NH$_4$F, HF and water is used
- HF-contained etchants and water wet SiO$_2$ but not Si: hydrophobic condition is the indication of the completion of etching of SiO$_2$. 
**Silicon Dioxide Wet Etch**

HF used.

Good selectivity for oxide, Si almost not attacked

Pure (49%) HF etches too fast (300 A/s) at ambient temp.

Use buffer and lower concentration to control etch rate

Ammoniumfluoride buffer common: BOE

Use surfactant for good surface coverage (e.g. Triton X100)
Silox Wet Etch

Silox is SiO$_2$ just as the oxide grown from the bulk. Silox, however, refers to deposited and not grown oxide. It etches faster and usually aluminum or copper layers are present, when it is deposited. BOE attacks these metals and can therefore not be used. Metal degradation can be seen as brown/spotty metal pads. Etch silox with a mixture of ammoniumfluoride and acetic acid (1:2)
Si$_3$N$_4$ etching

- Can be used as insulator between insulators
- Can be used as mask for ion implantation and diffusion
- Can be used as dielectric materials for MOSFET-based devices
- Grown by chemical vapor deposition
- Using boiling phosphoric acid (H$_3$PO$_4$) (150°C-180°C)
- Etching chemistry
- Cannot be etched with HF, while H$_3$PO$_4$ cannot effectively etch SiO$_2$, so SiO$_2$ and Si$_3$N$_4$ can be etch stop for each other

\[ H_3PO_4 + Si_3N_4 + H_2O \approx NO + NO_3^- + H_2PO_4^- + H_2SiO_3 \]
Silicon Nitrite Wet Etch

Used similar to silox as passivation layer

Very hard and resistant, etches slowly only.

Use phosphoric acid at elevated temp. (180C)

Problem 1: fumes have to be contained as they are abundant and poisonous.

Problem 2: the resist is rapidly dissolved. It has to be etched in a two step way with first deposition an oxide layer that works as mask

Dry etching more common
Aluminum Etch

Active ingredient: Phosphoric acid in water

Phosphoric Acid causes the formation of bubbles in the liquid. These can prevent etching of underlying spots causing “snowflakes”.


Wetting agent (surfactant) often needed
**Wet Etching**

Spray application of the etching solution instead of immersion allows better concentration and contamination control.

Vapor deposition is even cleaner, however only works, if etchants form homogeneous vapor. Usually HF used.

Both systems require tight containment of the toxic etchant. This is a safety concern!
Disadvantages of wet etching

- Most wet etching is isotropic, resulting in sloped sidewalls or undercutting
- Wet etching is limited to larger pattern sizes, shall be very cautious for submicron process, for line width comparable with film thickness, the etching is not tolerable
- A wet-etch process requires rinse and dry steps
- Wet chemicals are hazardous and/or toxic, needing proper disposal steps
- Wet processes represent a contamination potential
Dry Etching

Why dry etching?

- WE is limited to pattern sizes above 3mm
- WE is isotropic causing underetching
- WE requires rinse and dry
- WE chemicals are hazardous
- WE has contamination risk
- WE causes strong undercutting if resist lifts
Dry etching: three types

**PHYSICAL SPUTTERING**
(and ion beam milling)
- Physical momentum transfer
- Directional etch (anisotropic) possible
- Poor selectivity
- Radiation damage possible

**RIE (Halocarbon Gas)**
- Physical (ion) and chemical
- Directional
- More selective than sputtering

**PLASMA ETCHING**
- Chemical, thus faster by 10-1000X
- Isotropic
- More selective
- Less prone to radiation damage
**Plasma Dry Etching**

Principle of operation:
Expose wafers to CF$_4$ and oxygen.
Plasma supplies the energy for the formations of volatile fluorides.
Plasma is generated by RF discharge.
Controlled atmosphere required: usually done in a chamber that is first evacuated and then filled with the reactive gas.
Plasma etching sequence (Chemical process)

13.56MHz

Gas in

Electron impact reactions

Gas flow

Diffusion of reactant

Diffusion of byproduct desorption

Absorption

Chemical reaction

Gaseous byproducts

Substrate

Pump out
**Barrel Plasma Etcher**

Poor uniformity (wafers shadow each other off)
Radiation damage to wafers from plasma
Isotropic etching -> tapered walls

_ECE541/ME541 Microelectronic Fabrication Techniques_
**Barrel Plasma Etcher with Shield**

Perforated metal shield separates the plasma from the wafers

Reactive species have to travel to wafers

Reduces radiation damage and charging effects
Planar Plasma Etcher

Commercially Used

Uniformity is increased by rotation of wafers
Radiation damage low due to separation of plasma and wafers
Etching process very directional
Single wafer processing possible
Plasma Etching Figures-of-Merit

Etch Rate
Radiation Damage
Selectivity
Particulate Contamination
Post-Etch Corrosion
Etch Rate

Determined by system design (geometry)

Ion density (usually $10^{10} - 10^{12}$ per cm$^3$)

Pressure (high pressure increases etch rate but decreases anisotropy by intermolecular collision)

0.5-70 hPa typical

Typical etch rates are 600-2000 A/min
Radiation Damage

Electromagnetic radiation can effect all parts of a chip
Charged particles especially affect dielectrics (oxides, photoresist), where the charge is not neutralized.
Dielectric breakdown and photoresist hardening beyond stripping is the consequence
Prevent by low ion density and large distance between plasma and wafer.
Selectivity

In an ideal situation no selectivity would be necessary

Real process require selectivity because of

- non-perfect uniformity of deposited layers
- slanted underlying layers
- microloading in very small structures
- designed overetch can be up to 200% for oxide etches and 50-80% for metal etches

- two selectivity issues: photoresist, underlying layer
- issue: aspect ratio of 4:1 often occurs in modern devices

Try etching slower towards the end. Endpoint analysis by mass spectrometry possible.
Contamination/Post-etch corrosion

Post-etch corrosions is caused by halogens remnant on the wafer surface after etching. Fluorine more likely to cause problems than chlorine.

Remove by wet resist stripping
**Ion beam etching/ion milling/sputtering**

Argon ions are ionized and accelerated onto a negatively charged wafer where there impact removes material.

No chemical reactions; just momentum transfer.

Very directional/anisotropic

Poor selectivity

Charging and radiation damage is problem
Ion milling (Physical process)

- Electron impact reactions to generate Ar ions
- 13.56MHz
- Argon gas in
- Pump out
Reactive ion etching (RIE)

Combination of both processes:

Molecules are ionized to a reactive state and electrostatically accelerated onto the sample

High selectivity for oxide/silicon (35:1) compared to (10:1) for planar plasma etch.

Method with most industrial applications

Important for Nanotechnology

Through-Wafer holes are possible
Reactive ion etching sequence (Both physical and chemical)

Diagram:
- Gas in
- Electron impact reactions
- Diffusion of reactant
- Chemical reaction
- Gaseous byproducts
- Diffusion of byproduct desorption
- Substrate
- Pump out
- 13.56MHz
- \(-V\)
Etching gases and etching products

Table 14-2 EXAMPLES OF SOLID-GAS SYSTEMS USED IN PLASMA ETCHING

<table>
<thead>
<tr>
<th>SOLID</th>
<th>ETCH GAS</th>
<th>ETCH PRODUCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si, SiO₂, Si₃N₄</td>
<td>CF₄, SF₆, NF₃</td>
<td>SiF₄</td>
</tr>
<tr>
<td>Si</td>
<td>Cl₂, CC₁₂F₂</td>
<td>SiCl₂, SiCl₄</td>
</tr>
<tr>
<td>Al</td>
<td>BC₁₃, CC₁₄, SiCl₄, Cl₂</td>
<td>AlCl₃, Al₂Cl₆</td>
</tr>
<tr>
<td>Organic Solids</td>
<td>O₂</td>
<td>CO, CO₂, H₂O</td>
</tr>
<tr>
<td>Refractory Metals (W, Ta, Mo...)</td>
<td>O₂ + CF₄</td>
<td>CO, CO₂, HF</td>
</tr>
<tr>
<td></td>
<td>CF₄</td>
<td>WF₆, ...</td>
</tr>
</tbody>
</table>

For example:
To etch Si:

\[
CF₄ \rightarrow F^* + CF₃
\]

\[
CF₄ + e \leftrightarrow CF₃^+ + F^* + 2e
\]

\[
Si + 4F^* \rightarrow SiF₄ \uparrow
\]

F* are Fluorine atoms with electrons

To etch Al:

\[
CCl₄ + e \leftrightarrow CCl₃⁺ + Cl^* + 2e
\]

\[
Al + 3Cl^* \rightarrow AlCl₃ \uparrow
\]

To etch photoresist:

\[
C_xH_yO_z + O_2 \rightarrow CO_x
\]

\[
H₂O_x
\]
Bosch DRIE (Deep RIE) Process

Process developed by Robert Bosch

Switching between etching and passivation cycle

Passivation mechanism:
Conformal deposition of $C_4F_8$

Etching Mechanism:
Directional etching via radicals dissociated from $SF_6$ in high density plasma.
Results

Sample etch profiles for Bosch process.

High aspect ratio etches are possible.
**Resists and Dry Etching**

Thermal problems: temperatures during etch can be as high as 200C.

Resist is baked hard and can melt and expand. Edge definition lost.

Resist can be oxidized by oxygen from SiO₂, which turns it into volatile CO, CO₂, water and creates holes.

Formation of sidewall polymers, which cause problems during resist removal (stripping)
## Resist stripping

<table>
<thead>
<tr>
<th>Wet stripping</th>
<th>Dry stripping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly precise</td>
<td>No chemicals/hoods</td>
</tr>
<tr>
<td>Gentle to the underlying substrate</td>
<td>Little contamination problems</td>
</tr>
<tr>
<td>Used FEOL (front end of the line)</td>
<td>Uses same equipment as step before/easy combination</td>
</tr>
<tr>
<td>Cost effective</td>
<td>Used BEOL (Back end of the line)</td>
</tr>
<tr>
<td>Removes metallic ions and halogens</td>
<td></td>
</tr>
</tbody>
</table>
Choice of the right stripping reagent

Positive resists can be stripped with solvents or acids, negative ones require acids.

Most acids are incompatible with metallized surfaces. Exceptions are some organic acids such as acetic acid. These are less reactive and require higher temperatures.

Most common wet strippers are mixtures of sulfuric acid with some oxidant such as hydrogen peroxide or ammonium persulfate. These can be used for oxides and nitrites but not for metal surfaces!

Nitric acid can be used as oxidant, but its color masks other problems.
Stripping of metallized surfaces

Phenolic strippers

J-100 Industries Chem.
Mixture of sulfonic acid, halogenated solvent and phenol
toxic, not used anymore

Solvent/Amine stripper

For positive resists only

Solvents: N-methyl pyrrolidine (NMP) (most common),
dimethylsulfoxide (DMSO), dimethylformamide (DMF),
dimethylacetamide (DMAC)

Drain-dumpable

Heatable for faster removal/hard-baked films

Acetone works, but fire hazard for industrial applications
**Wet strippers summary**

<table>
<thead>
<tr>
<th>Stripper Chemistry</th>
<th>Strip Temperature (Centigrade)</th>
<th>Surface Oxide</th>
<th>Metallized</th>
<th>Resist Polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid+oxidant</td>
<td>125</td>
<td>X</td>
<td></td>
<td>+/-</td>
</tr>
<tr>
<td>Organic Acids</td>
<td>90-110</td>
<td>X</td>
<td>X</td>
<td>+/-</td>
</tr>
<tr>
<td>Chronic/Sulfuric</td>
<td>20</td>
<td>X</td>
<td></td>
<td>+/-</td>
</tr>
<tr>
<td>Solvents:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMP/Alkanolamine</td>
<td>95</td>
<td></td>
<td>X</td>
<td>+</td>
</tr>
<tr>
<td>DMSO/Monoanolamine</td>
<td>95</td>
<td></td>
<td>X</td>
<td>+</td>
</tr>
<tr>
<td>DMAC/Diethanolamine</td>
<td>100</td>
<td></td>
<td>X</td>
<td>+</td>
</tr>
<tr>
<td>Hydroxylamine (HDA)</td>
<td>65</td>
<td></td>
<td>X</td>
<td>+</td>
</tr>
</tbody>
</table>
Dry Stripping

Same as plasma etching, but oxygen is used as gas.

\[ \text{C}_x\text{H}_y\text{(resist)} + \text{O}_2 \text{(plasma energized)} \rightarrow \text{CO} \text{(gas)} + \text{CO}_2 \text{(gas)} + \text{H}_2\text{O} \]

A plasma dry stripping process is called ashing

No removal of metal ions and potential radiation damage

BEOL process

Required if metal halides might have been created in plasma etching to transform them in oxides, which can be wet removed subsequently

Required after ion implantation, as film is too crusted to be removed by wet process only. A wet stripping process is used after the dry one.
# Wet and Dry Etching

<table>
<thead>
<tr>
<th>Method</th>
<th>Wet</th>
<th>Dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment</td>
<td>Chemical solutions</td>
<td>Plasma or ion beam</td>
</tr>
<tr>
<td>Wet bench</td>
<td>Etching system in vacuum</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Advantages</th>
<th>1) Low cost, easy to implement</th>
<th>1) Capable of defining small feature size (&lt;100 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2) High etch rate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3) Good selectivity for most mask materials</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Disadvantages</th>
<th>1) Inadequate for defining feature size &lt; 1 um</th>
<th>1) High cost</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2) Potential of chemical handling hazards</td>
<td>2) Low through put</td>
</tr>
<tr>
<td></td>
<td>3) Wafer contamination</td>
<td>3) Poor selectivity</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Directionality</th>
<th>Isotropic except for etching crystalline materials</th>
<th>Anisotropic</th>
</tr>
</thead>
</table>
Directional, Isotropic, and Anisotropic Etching

Orientation dependent Si etching pattern profile
(a) on (100) Si; (b) on (110) Si
Enchant: 23.4 wt% KOH, 13.3wt% isopropyl, 63% wt% H2O at 80°C
Etch rate: 100 times faster along (100) planes than along (111) planes

(a) Isotropic etching
(b) Anisotropic etching
Dry etching: three types

**PHYSICAL SPUTTERING**
(and Ion Beam Milling)

- Physical momentum transfer
- Directional etch (anisotropic) possible
- Poor selectivity
- Radiation damage possible

**RIE (Halocarbon Gas)**

- Physical (ion) and chemical
- Directional
- More selective than sputtering

**PLASMA ETCHING**

- Chemical, thus faster by 10-1000X
- Isotropic
- More selective
- Less prone to radiation damage
Dry etching: three types

PHYSICAL SPUTTERING
(and Ion Beam Milling)
- Physical momentum transfer
- Directional etch (anisotropic) possible
- Poor selectivity
- Radiation damage possible

RIE (Halocarbon Gas)
- Physical (ion) and chemical
- Directional
- More selective than sputtering

PLASMA ETCHING
- Chemical, thus faster by 10-1000X
- Isotropic
- More selective
- Less prone to radiation damage
Plasma Definition

- Plasma: partially ionized gas consisting of equal numbers of positive and negative charges, and different number of un-ionized neutral molecules.

Typical parameter values

**Neutrals**

m = 6.6x10^{-23} g
T = 20°C = 293 K = 1/40eV
c = 4.0 x10^4 cm/sec

**Ions**

m_i = 6.6x10^{-23} g
T_i = 500 K = 0.04eV
c_i = 5.2 x10^4 cm/sec

**Electrons**

m_e = 9.1x10^{-28} g
T_e = 23200 K = 2eV
c_e = 9.5 x10^7 cm/sec

c = (8kT/πm)^{1/2}
General Information

- **Vacuum**
  - number density of gases
    - at 1 mTorr, $3.5 \times 10^{12}$ molecules/cm$^3$
    - or 35 molecules/µm$^3$
  - mean free path $\lambda$ (cm)
    - at 1 mTorr, $\lambda = 5$ cm

- **Electron (e)**
  - mass ($m_e$) = $9.1 \times 10^{-28}$ gm
  - charge ($e$) = $1.6 \times 10^{-19}$ coulomb

- **Proton (H$^+$)**
  - mass = $1.67 \times 10^{-24}$ gm = $1837 \ m_e$
  - charge ($e$) = $1.6 \times 10^{-19}$ coulomb

- **Neutral Molecule**
  - 1 or more atoms with fully satisfied bonding, uncharged
  - can be chemically active
  - e.g. Cl$_2$, F$_2$, CF$_4$, SiF$_4$

- **Radical**
  - 1 or more atoms with unsatisfied chemical bonding, uncharged
  - very chemically active
  - e.g. F, O, OH, CF$_x$ ($x = 1, 2, 3$)
Comparison of Low Density and High Density Plasma Reactors

- Relative Concentrations of Species in Low Density Plasma Reactor

- Relative Concentrations of Species in High Density Plasma Reactor
Main Collision Processes in Plasma

- Ionization
  \[ e + \text{Ar} \rightarrow 2e + \text{Ar}^+ \]
- Excitation
  \[ e + \text{Ar} \rightarrow e + \text{Ar}^+ \]
- Relaxation
  \[ e + \text{Ar}^+ \rightarrow e + \text{Ar} + \text{photon} \]
- Recombination
  \[ e + \text{Ar}^+ \rightarrow \text{Ar} \]
- Dissociation
  \[ e + \text{O}_2 \rightarrow \text{O} + \text{O} + e \]
  \[ e + \text{CF}_4 \rightarrow \text{CF}_3 + \text{F} + e \]
- Dissociation and Ionization
  \[ e + \text{CF}_4 \rightarrow \text{CF}_3^+ + \text{F} + 2e \]
## Gas-Solid Systems

<table>
<thead>
<tr>
<th>Solid</th>
<th>Etch Gas</th>
<th>Etch Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>CF₄, Cl₂, HBr, SF₆, NF₃</td>
<td>SiF₄, SiCl₄, SiCl₂, SiBr₄</td>
</tr>
<tr>
<td>SiO₂, Si₃N₄</td>
<td>CF₄, C₄F₈, CHF₃, SF₆</td>
<td>SiF₄, CO, O₂, N₂, H₂</td>
</tr>
<tr>
<td>Al</td>
<td>SCL₂/Cl₂</td>
<td>Al₂Cl₆, AlCl₃</td>
</tr>
<tr>
<td>W, Ta, Nb, Mo</td>
<td>CF₄, Cl₂, HBr, SF₆, NF₃</td>
<td>WF₆, WCl₆, WBr₆</td>
</tr>
<tr>
<td>Ti, TiN</td>
<td>Cl₂, CF₄</td>
<td>TiCl₄, TiF₄</td>
</tr>
<tr>
<td>Organic Solids</td>
<td>O₂, H₂O, O₂/CF₄</td>
<td>CO, CO₂, H₂O, HF, H₂</td>
</tr>
<tr>
<td>GaAs &amp; III-V</td>
<td>Cl₂/Ar, HBr,</td>
<td>Ga₂Cl₆, AsCl₃</td>
</tr>
<tr>
<td>CdTe &amp; II-VI</td>
<td>CH₄/H₂</td>
<td>Cd(CH₃)₂, H₂Te</td>
</tr>
<tr>
<td>Cr</td>
<td>Cl₂/O₂</td>
<td>CrO₂Cl₂</td>
</tr>
</tbody>
</table>
## Boiling Points of Typical Etch Products

<table>
<thead>
<tr>
<th>Element</th>
<th>Chlorides</th>
<th>Boiling Point (°C)</th>
<th>Fluorides</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>AlCl3</td>
<td>177.8</td>
<td>AlF3</td>
<td>1291</td>
</tr>
<tr>
<td>As</td>
<td>AsCl3</td>
<td>130.2</td>
<td>AsF3</td>
<td>53</td>
</tr>
<tr>
<td>Cr</td>
<td>CrO2Cl2</td>
<td>117</td>
<td>CrF2</td>
<td>&gt;1300</td>
</tr>
<tr>
<td></td>
<td>CrCl3</td>
<td>1300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>CuCl</td>
<td>1490</td>
<td>CuF</td>
<td>1100</td>
</tr>
<tr>
<td>Ga</td>
<td>GaCl3</td>
<td>201.3</td>
<td>GaF3</td>
<td>&gt;1200</td>
</tr>
<tr>
<td>In</td>
<td>InCl3</td>
<td>300</td>
<td>InF3</td>
<td>&gt;1200</td>
</tr>
<tr>
<td>Mo</td>
<td>MoCl5</td>
<td>268</td>
<td>MoF6</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>MoOCl3</td>
<td>100</td>
<td>MoF5</td>
<td>213.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MoO2F2</td>
<td>270</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MoOF4</td>
<td>180</td>
</tr>
<tr>
<td>Nb</td>
<td>NbCl5</td>
<td>254</td>
<td>NbF4</td>
<td>236</td>
</tr>
<tr>
<td></td>
<td>NbOCl3</td>
<td>335</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>SiCl4</td>
<td>57.6</td>
<td>SiF4</td>
<td>-86</td>
</tr>
<tr>
<td>Ta</td>
<td>TaCl5</td>
<td>242</td>
<td>TaF5</td>
<td>229.5</td>
</tr>
<tr>
<td>Ti</td>
<td>TiCl4</td>
<td>136.4</td>
<td>TiF4</td>
<td>284</td>
</tr>
<tr>
<td>W</td>
<td>WC16</td>
<td>346.7</td>
<td>WF6</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>WC15</td>
<td>275.6</td>
<td>WOF4</td>
<td>187.5</td>
</tr>
<tr>
<td></td>
<td>WC14</td>
<td>227.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Bond Energies and Ionization Potentials

### Bond Energies in eV

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O</td>
<td>11.2</td>
</tr>
<tr>
<td>N-N</td>
<td>9.86</td>
</tr>
<tr>
<td>Si-O</td>
<td>8.17</td>
</tr>
<tr>
<td>C-N</td>
<td>8.0</td>
</tr>
<tr>
<td>H-F</td>
<td>5.87</td>
</tr>
<tr>
<td>C-F</td>
<td>5.57</td>
</tr>
<tr>
<td>Si-F</td>
<td>5.14</td>
</tr>
<tr>
<td>O-O</td>
<td>5.17</td>
</tr>
<tr>
<td>H-H</td>
<td>4.96</td>
</tr>
<tr>
<td>Si-Cl</td>
<td>4.57</td>
</tr>
<tr>
<td>H-O, H-Cl</td>
<td>4.45</td>
</tr>
<tr>
<td>C-Cl</td>
<td>4.04</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>2.52</td>
</tr>
<tr>
<td>F-F</td>
<td>1.61</td>
</tr>
</tbody>
</table>

### Ionization Potentials

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>24.6</td>
</tr>
<tr>
<td>Ne</td>
<td>21.6</td>
</tr>
<tr>
<td>F</td>
<td>17.4</td>
</tr>
<tr>
<td>Ar, HF</td>
<td>15.8</td>
</tr>
<tr>
<td>F2</td>
<td>15.7</td>
</tr>
<tr>
<td>CF4, N2</td>
<td>15.6</td>
</tr>
<tr>
<td>H2</td>
<td>15.4</td>
</tr>
<tr>
<td>N</td>
<td>14.5</td>
</tr>
<tr>
<td>Kr, CO</td>
<td>14.0</td>
</tr>
<tr>
<td>CO2</td>
<td>13.8</td>
</tr>
<tr>
<td>H, O</td>
<td>13.6</td>
</tr>
<tr>
<td>Cl</td>
<td>13.0</td>
</tr>
<tr>
<td>HCl</td>
<td>12.7</td>
</tr>
<tr>
<td>H2O, CH4</td>
<td>12.6</td>
</tr>
<tr>
<td>Xe, O2</td>
<td>12.1</td>
</tr>
<tr>
<td>Br</td>
<td>11.8</td>
</tr>
<tr>
<td>HBr</td>
<td>11.6</td>
</tr>
<tr>
<td>Cl2, CC14</td>
<td>11.5</td>
</tr>
<tr>
<td>(H)</td>
<td>(He)</td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
</tr>
<tr>
<td>Li</td>
<td>Be</td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
</tr>
<tr>
<td>Fr</td>
<td>Ra</td>
</tr>
<tr>
<td>RF</td>
<td>Db</td>
</tr>
</tbody>
</table>

(X) = gaseous; X = etchable at or near room T; X = not known to be etchable
Neutral/Ion Flux Ratio Effect On Etch Profile

<table>
<thead>
<tr>
<th>Parameter</th>
<th>F atom flux</th>
<th>Ion energy</th>
<th>Side wall directionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>RF power</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Etch area</td>
<td>↑</td>
<td>No change</td>
<td>↑</td>
</tr>
<tr>
<td>Add H2 (F/C)</td>
<td>↓</td>
<td>No change</td>
<td>↑</td>
</tr>
<tr>
<td>Add O2 (F/C)</td>
<td>↓</td>
<td>No change</td>
<td>↓</td>
</tr>
</tbody>
</table>
Etch Gas Effect On Etch Profile

Boiling Temperature

<table>
<thead>
<tr>
<th>Gas</th>
<th>Boiling Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>-111.6 °C</td>
</tr>
<tr>
<td>SiF₄</td>
<td>-95.7 °C</td>
</tr>
<tr>
<td>SiHCl₃</td>
<td>31.7 °C</td>
</tr>
<tr>
<td>SiCl₂</td>
<td>56.7 °C</td>
</tr>
<tr>
<td>Si₂OCl₆</td>
<td>135.5 °C</td>
</tr>
</tbody>
</table>
Highlight of RIE

- In a typical plasma reactor
  - Neutral Molecules density: $1 \times 10^{16} / \text{cm}^3$
  - Radicals: $1 \times 10^{14}$
  - Charge particles: $1 \times 10^9$ (low) or $1 \times 10^{11}$ (high)

- Volatile compounds formation is essential for reactive ion etching.

- Ion-assisted gas-surface chemistry enhanced etch rate significantly. It is responsible for the anisotropic etching obtained in RIE processes.
Pattern Transfer: Etching vs. Lift-off

ECE541/ME541 Microelectronic Fabrication Techniques
ECE 541/ME 541
Microelectronic Fabrication Techniques

MW 4:00-5:15 pm

III-V Etching

Zheng Yang

ERF 3017, email: yangzhen@uic.edu, MW 5:15-6:00 pm
UNAXIS ICP RIE system at Harvard

- **Process characteristics:** high plasma density, low process pressure, high etch rate, good etch uniformity, and low energy ion damage
- **Process temperature:** 15 – 200 °C
- **Sample size:** 6” or smaller
- **Available gases:** HBr, Cl2, BCl3, CH4, H2, Ar, N2, and O2
- **~ 2 minutes sample loading & unloading time**
- **Computer controlled operation**
Established Processes with Unaxis

- GaAs Micro- and Nano- Trenches
- AlGaAs Microtrenches
- InP Nanophotonic Crystal
- InP (10 – 20 μm deep)
- InP/(AlInAs-GaInAs multi-layers)/InP (10 – 20 μm deep)
GaAs Microtrenches

Chemistry: BCl3, Cl2  
Mask: Photoresist  
Selectivity: 3.2  
Etch rate: 0.8 um/min

clean & smooth etch surface, 85 degree side wall angle, good selectivity to photo resist
AlGaAs Microtrenches

Chemistry:  BC\textsubscript{13}, Cl\textsubscript{2}
Mask:  Photoresist
Selectivity:  > 3:1
Etch rate:  0.7 \textmu m/min

Clean & smooth etch surface, > 85 degree side wall angle, good selectivity to photo resist
GaAs Nanotrenches

Chemistry: BCl3, Ar, N2
Mask: PMMA
Selectivity: 1.22
Etch rate: 0.5 μm/min

This process was used to etch nano-trenches and -holes and resulted in clean & smooth etch surface, good selectivity to PMMA, and 85 degree side wall.
InP Nanophotonic Crystal

Chemistry: BCl3, CH4, Ar
Temperature: 160°C
Mask: Si3N4
Selectivity: > 5:1
Etch rate: ~ 1.0 um/min
InP Etch Processes

<table>
<thead>
<tr>
<th>Chemistry:</th>
<th>HBr, N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature:</td>
<td>180°C</td>
</tr>
<tr>
<td>Mask:</td>
<td>SU8</td>
</tr>
<tr>
<td>Selectivity:</td>
<td>&gt; 10:1</td>
</tr>
<tr>
<td>Etch rate:</td>
<td>~ 2.0 μm/min</td>
</tr>
</tbody>
</table>

clean & smooth etch surface, 10 – 15 μm deep etch, vertical side wall, greater than 10:1 selectivity to Si3N4 or SU-8
# InP Etch Processes

<table>
<thead>
<tr>
<th>Substrate:</th>
<th>InP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry:</td>
<td>BCl3, CH4, Ar</td>
</tr>
<tr>
<td>Temperature:</td>
<td>160°C</td>
</tr>
<tr>
<td>Mask:</td>
<td>Si3N4 or SU-8</td>
</tr>
<tr>
<td>Etch rate:</td>
<td>~1.0 μm/min</td>
</tr>
</tbody>
</table>

**clean & smooth etch surface, 10 – 15 μm deep etch, vertical side wall**
III-V etching

- III-V etching processes demonstrated high etch rate, smooth etched surface, 85-90 degree sidewall angle, good selectivity to PMMA, Si3N4, and SU-8 mask materials.
- Conductivity of sample carrier affects etching results significantly.
- E-beam dosage is a factor that influence sidewall angles.
- Surface cleaning before etching is critical to obtain clean and smooth etched surface.