ECE 541/ME 541
Microelectronic Fabrication Techniques

MW 4:00-5:15 pm

Etching

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Major Fabrication Steps in MOS Process Flow

- Oxidation (Field oxide)
- Photoresist Coating
- Mask-Wafer Alignment and Exposure
- Exposed Photoresist
- Photoresist Develop
- Oxide Etch
- Photoresist Strip
- Oxidation (Gate oxide)
- Polysilicon Deposition
- Polysilicon Mask and Etch
- Ion Implantation
- Active Regions
- Nitride Deposition
- Contact Etch
- Metal Deposition and Etch

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

Etch

Wet
  - Immersion
  - Spray

Dry
  - Plasma
    - Ion Milling
      - Barrel
      - Planar
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

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

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

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

Reactant diffusion  Product diffusion

Resist

Surface reaction

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, “Glacial”</td>
<td>CH₃COOH</td>
<td>60.0</td>
<td>99%</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 Å/MIN</th>
<th>METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiO}_2$</td>
<td>Room</td>
<td>700</td>
<td>Dip &amp; wetting agent predip</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>Room</td>
<td>1000</td>
<td>Dip</td>
</tr>
<tr>
<td>Vapox</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>Room</td>
<td>1000</td>
<td>Dip</td>
</tr>
<tr>
<td>Vapox</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>Room</td>
<td>1000</td>
<td>Dip</td>
</tr>
<tr>
<td>Wetting Agent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiN$_2$</td>
<td>Room</td>
<td>1000</td>
<td>Dip</td>
</tr>
<tr>
<td>POLYSi</td>
<td>Room</td>
<td>1000</td>
<td>Dip</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$_2$. 

ECE541/ME541 Microelectronic Fabrication Techniques
**Silicon Dioxide Wet Etch**

HF used.

Good selectivity for oxdie, 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)
Si₃N₄ 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 (H₃PO₄) (150°C-180°C)
- Etching chemistry
- Cannot be etched with HF, while H₃PO₄ cannot effectively etch SiO₂, so SiO₂ and Si₃N₄ can be etch stop for each other

\[ H₃PO₄ + Si₃N₄ + H₂O \approx NO + NO_3^- + H₂PO_4^- + H₂SiO₃ \]
Silicon Nitrite Wet Etch

Used similar to silox as passivation layer
Very hard and resistant, etches slowly only.

Use phosphoric acid at elevated temp. (180°C)

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**
- 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:
Exposure of wafers to CF$_4$ and oxygen.
Plasma supplies the energy for the formation 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

Substrate

Gas flow

diffusion of reactant

diffusion of by product desorption

absorption

chemical reaction

gaseous by products

Pump out
Barrel Plasma Etcher

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

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

Commercially Used
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 affect 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 processes require selectivity because of:

- non-perfect uniformity of deposited layers
- slanted underlying layers
- microlading 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 the impact removes material.

No chemical reactions; just momentum transfer.

Very directional/anisotropic

Poor selectivity

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

Electron impact reactions to generate Ar ions

13.56MHz

Argon gas in

PR

Substrate

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)

13.56MHz
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, CCl₂F₂</td>
<td>SiCl₂, SiCl₄</td>
</tr>
<tr>
<td>Al</td>
<td>BCl₃, CCl₄, 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:

\[ C_x H_y O_z + O_2 \leftrightarrow CO_x \]

\[ \rightarrow HO_x \]
**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 SiO$_2$, which turns it into volatile CO, CO$_2$, water and creates holes.

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

Wet stripping

Highly precise
Gentle to the underlying substrate
Used FEOL (front end of the line)
Cost effective
Removes metallic ions and halogens
Low temp.

Dry stripping

No chemicals/hoods
Little contamination problems
Uses same equipment as step before/easy combination
Used BEOL (Back end of the line)
**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), dimethylforamide (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>X</td>
<td>+/-</td>
</tr>
<tr>
<td>Organic Acids</td>
<td>90-110</td>
<td>X</td>
<td></td>
<td>+/-</td>
</tr>
<tr>
<td>Chromic/Sulfuric Solvents</td>
<td>20</td>
<td>X</td>
<td>X</td>
<td>+/-</td>
</tr>
<tr>
<td>NMP/Alkanolamine</td>
<td>95</td>
<td></td>
<td>X</td>
<td>+</td>
</tr>
<tr>
<td>DMSO/Monoethanolamine</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.

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>Wet bench</td>
<td>Etching system in vacuum</td>
</tr>
</tbody>
</table>
| Advantages| 1) Low cost, easy to implement  
2) High etch rate  
3) Good selectivity for most mask materials | 1) Capable of defining small feature size (<100 nm) |
| Disadvantages| 1) Inadequate for defining feature size < 1 um  
2) Potential of chemical handling hazards  
3) Wafer contamination | 1) High cost  
2) Low through put  
3) Poor selectivity  
4) Potential radiation damage |
| Directionality| Isotropic except for etching crystalline materials | Anisotropic |
Directional, Isotropic, and Anisotropic Etching

Orientation dependent Si etching pattern profile
(a) on (100) Si; (b) on (110) Si

Enchant: 23.4 wt% KOH, 13.3 wt% 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
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**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*

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutrals</td>
<td>$m = 6.6 \times 10^{-23}$ g</td>
</tr>
<tr>
<td></td>
<td>$T = 20^\circ C = 293$ K = 1/40eV</td>
</tr>
<tr>
<td></td>
<td>$c = 4.0 \times 10^{4}$ cm/sec</td>
</tr>
<tr>
<td>Ions</td>
<td>$m_i = 6.6 \times 10^{-23}$ g</td>
</tr>
<tr>
<td></td>
<td>$T_i = 500$ K = 0.04eV</td>
</tr>
<tr>
<td></td>
<td>$c_i = 5.2 \times 10^{4}$ cm/sec</td>
</tr>
<tr>
<td>Electrons</td>
<td>$m_e = 9.1 \times 10^{-28}$ g</td>
</tr>
<tr>
<td></td>
<td>$T_e = 23200$ K = 2eV</td>
</tr>
<tr>
<td></td>
<td>$c_e = 9.5 \times 10^{7}$ cm/sec</td>
</tr>
</tbody>
</table>

$c = (8kT/\pi m)^{1/2}$
General Information

- **Vacuum**
  - number density of gases
    - at 1 mTorr, $3.5 \times 10^{13}$ 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**
  \[ e + Ar \rightarrow 2e + Ar^+ \]

- **Excitation**
  \[ e + Ar \rightarrow e + Ar^* \]

- **Relaxation**
  \[ e + Ar^* \rightarrow e + Ar + photon \]

- **Recombination**
  \[ e + Ar^+ \rightarrow Ar \]

- **Dissociation**
  \[ e + O_2 \rightarrow O + O + e \]
  \[ e + CF_4 \rightarrow CF_3 + F + e \]

- **Dissociation and Ionization**
  \[ e + CF_4 \rightarrow CF_3^+ + F + 2e \]
## 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>SCL₃/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>
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<td>CrO₂Cl₂</td>
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<td></td>
<td>MoOF₄</td>
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<tr>
<td></td>
<td>NbOCl₃</td>
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<td>TaF₅</td>
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<td>Ti</td>
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<td>136.4</td>
<td>TiF₄</td>
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<tr>
<td>W</td>
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<td>WF₆</td>
<td>17.5</td>
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<tr>
<td>WC₁₅</td>
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<td>WOF₄</td>
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<tr>
<td>WOCl₄</td>
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# Bond Energies and Ionization Potentials

## Bond Energies in eV

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

## Ionization Potentials

<table>
<thead>
<tr>
<th>Substance</th>
<th>Potential (eV)</th>
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<tr>
<td>He</td>
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<tr>
<td>Ne</td>
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<tr>
<td>F</td>
<td>17.4</td>
</tr>
<tr>
<td>Ar, HF</td>
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</tr>
<tr>
<td>F2</td>
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<tr>
<td>CF4, N2</td>
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<tr>
<td>H2</td>
<td>15.4</td>
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<tr>
<td>N</td>
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<tr>
<td>Kr, CO</td>
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<tr>
<td>CO2</td>
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<td>H, O</td>
<td>13.6</td>
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<tr>
<td>Cl</td>
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<tr>
<td>HCl</td>
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<td>H2O, CH4</td>
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<tr>
<td>Xe, O2</td>
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<tr>
<td>Br</td>
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<tr>
<td>HBr</td>
<td>11.6</td>
</tr>
<tr>
<td>Cl2, CCl4</td>
<td>11.5</td>
</tr>
</tbody>
</table>
(X) – gaseous, X – etchable at or near room T; X – not known to be etchable

X – STS RIE, X – Unaxis, X – Nexx RIE and SouthBay
Neutral/Ion Flux Ratio Effect On Etch Profile

![Graph showing the relationship between L and W with N and V labels, and an arrow indicating the effect of F and C on W.]

<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>↓ No change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add O2 (F/C ↑)</td>
<td>↑ No change</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Etch Gas Effect On Etch Profile

Boiling Temperature

<table>
<thead>
<tr>
<th></th>
<th>Temperature</th>
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</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: $1 \times 10^{16}$ /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
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, BC13, 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, 85degree side wall angle, good selectivity to photo resist
**AlGaAs Microtrenches**

| Chemistry: | BC13, Cl2 |
| Mask:      | Photoresist |
| Selectivity: | > 3:1 |
| Etch rate: | 0.7 um/ min |

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

<table>
<thead>
<tr>
<th>Chemistry:</th>
<th>BCl3, Ar, N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mask:</td>
<td>PMMA</td>
</tr>
<tr>
<td>Selectivity:</td>
<td>1.22</td>
</tr>
<tr>
<td>Etch rate:</td>
<td>0.5 um/min</td>
</tr>
</tbody>
</table>

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: BC13, CH4, Ar
Temperature: 160°C
Mask: Si3N4
Selectivity: > 5:1
Etch rate: ≈ 1.0 μm/min
InP Etch Processes

Chemistry: HBr, N2  
Temperature: 180°C  
Mask: SU8  
Selectivity: > 10:1  
Etch rate: ~ 2.0 μm/min

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

Mask Material

Silicon Nitride

SU-8
InP Etch Processes

Substrate: InP
Chemistry: BCl₃, CH₄, Ar
Temperature: 160°C
Mask: Si₃N₄ or SU-8
Etch rate: ~ 1.0 µm/min

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.