Lithography Etching

- Etching transfers the pattern from the resist to the wafer layer
- Resist protects pattern area
- Etch removes unwanted material to define pattern

Etching Definitions

- **Isotropic Etching**: same in all direction
- **Anisotropic Etching**: direction sensitive
- Selectivity: etch rate difference between 2 materials
- Need strong selectivity from masking material (eg. photoresist)
- Also good selectivity for other layers below one being etch

![Image](image.png)

Fig. 4. A summary of wet chemically etched hole geometries which are commonly used in micromechanical devices. (a) Anisotropic etching on (100) surfaces. (b) Anisotropic etching on (110) surfaces. (c) Isotropic etching with agitation. (d) Isotropic etching without agitation. Adapted from S. Terry [29].
Two Major types of etching

- **Wet Etching**: Liquid acids/bases dissolves layer create pattern
  - Eg HF etches away the unprotected glass oxide
  - Most common for simple patterning >3 microns
  - Problem is isotropic etch – etches both down and to the side
  - Quick, cheap and fast

- **Dry Etching**: using plasma or gases (2 types)
  - Plasma etching (PE)
  - Reactive Ion Etching (RIE)
  - Used for advanced etching typically < 2 microns
  - Tends to be anisotropic – less side etch
  - Also for better differentiation between layers
Basic Wet Etch Process

- Diffusion of reactant to surface
- Surface Reaction (absorption, reaction, desorption)
- Diffusion of products from surface
- This same cycle also applies to Dry Etching
- The slowest of these limits the etching process
Rate Limiting Step

- Rate limiting: slowest step which limits the process
- **Diffusion limited**: reactant/product diffusion controlled
- How fast reactant (or product) can get to the surface
- Thus very agitation sensitive
- **Activation limited**: surface reaction controlled
- Reaction rate is usually Temperature sensitive

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

- \( R_0 \) = Rate constant (depends on reactant density)
- \( E_A \) = Activation energy (in eV)
- \( T \) = Temperature (Kelvin)
- \( K \) = Boltzman's constant: 1.38 x 10\(^{23}\) J/K = 8.62 x 10\(^5\) eV/K
- Called Arrhenius behavior
- Often plot against 1000/T for x axis and log rate on y
Typical Wet Etching Process

- Etch proceeds both vertically and horizontally
- Undercutting: material removed under the mask
- At etch end has undercut edges
- Etch proceeds at slower rate for etch stop material
- Long overetch creates significant undercut

---

Fig 10
Wetting of surface

- Hyrdophilic: water loving
- Wets the surface ie covers the surface
- Wetting of surface, angle $< 90^\circ$
- Hyrdophobic: water hating
- Glass surface is water hydrophilic: water balls up on it
- Water rolls off the surface
- Non-wetting of surface, angle $> 90^\circ$
- Silicon surface with no oxide layer is hydrophobic

![Diagram showing wetting contact angles](image)

*Wetting Contact Angles*

Non-Wetting $T_\theta > 90^\circ$, Wetting $T_\theta < 90^\circ$, Spreading $T_\theta = 0^\circ$
Common Chemicals used in Wet Etches

- HF used for glass/silicon etch
- Nitric Acid used in silicon etch
- Phosphoric for Aluminum etch
- Ammonium Fluoride in glass Buffered Oxide Etch
- Ammonium Hydroxide in RCA Clean
- Acetic Acid as buffer agent

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

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molecular weight</th>
<th>Concentration†</th>
<th>Dissociation constant‡</th>
</tr>
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<tbody>
<tr>
<td>Hydrofluoric acid</td>
<td>HF</td>
<td>20.0</td>
<td>49%</td>
<td>$3.53 \times 10^{-4}$</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>63.0</td>
<td>69.5%</td>
<td>(Strong acid)</td>
</tr>
<tr>
<td>Acetic acid, “Glacial”</td>
<td>H₄C₂O₂</td>
<td>60.0</td>
<td>99%</td>
<td>$1.76 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>CH₃COOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>98.1</td>
<td>98%</td>
<td>$1.20 \times 10^{-2}$</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>98.0</td>
<td>85%</td>
<td>$7.52 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ammonium fluoride</td>
<td>NH₄F</td>
<td>37.0</td>
<td>40%</td>
<td>Salt, dissolves in water</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>NH₄OH</td>
<td>35.05</td>
<td>29%</td>
<td>$1.79 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

† Concentration by weight, in water, as commonly supplied.
‡ At 25°C. For multibasic acids, the first dissociation constant is given.
Typical Wet Etchants

- Many recipe’s possible for each materials
- Important to note etch rate of material and other layers

<table>
<thead>
<tr>
<th>COMMON ETCHANT</th>
<th>ETCH TEMP</th>
<th>RATE Å/MIN</th>
<th>METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO: HF &amp; NH₄F</td>
<td>Room</td>
<td>700</td>
<td>Dip &amp; wetting agent pre-dip</td>
</tr>
<tr>
<td>SiO: HF &amp; NH₄F</td>
<td>Room</td>
<td>700</td>
<td>Dip &amp; wetting agent pre-dip</td>
</tr>
<tr>
<td>SiO: Acetic Acid &amp; NH₄F(2:1)</td>
<td>Room</td>
<td>1000</td>
<td>Dip</td>
</tr>
<tr>
<td>Aluminum H₃PO₄: 16</td>
<td>40 - 50°C</td>
<td>2000</td>
<td>a) Dip &amp; agitation, b) Spray</td>
</tr>
<tr>
<td>HNO₃: 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic: 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O: 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wetting Agent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si₃N₄ H₃PO₄</td>
<td>150 - 180°C</td>
<td>80</td>
<td>Dip</td>
</tr>
<tr>
<td>POLYSi HNO₃: 50</td>
<td>Room</td>
<td>1000</td>
<td>Dip</td>
</tr>
<tr>
<td>H₂O: 20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF: 3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 9.20 Summary of wet etching process.
Relative Chemical Purities

- Super pure grade good enough for chemistry but not microfab
- Must use electronic Grade

![Relative Chemical Purity Chart]

Fig 23
Chemical Impurities

- Electronic Grade impurities not only small
- Nill of deadly elements for devices eg Copper
- Also low dopants (Boron, Arsinic)

**Typical Impurity Levels in MOS Grade Chemicals**

**Table 27**

**J.T. Baker Chemicals**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CH₃COOH</th>
<th>NH₃OH</th>
<th>HCl</th>
<th>HF</th>
<th>H₂O₂</th>
<th>H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impurity Level in Parts Per Million</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.1</td>
<td>0.1</td>
<td>1.0</td>
<td>0.05</td>
<td>1.0</td>
<td>0.1</td>
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<tr>
<td>Ammonium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.005</td>
<td>0.05</td>
<td>0.005</td>
<td>0.03</td>
<td>0.01</td>
<td>0.005</td>
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<td>Barium</td>
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<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
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<td>1.0</td>
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<td>Boron</td>
<td>0.05</td>
<td>0.02</td>
<td>0.05</td>
<td>0.05</td>
<td>0.1</td>
<td>0.01</td>
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<tr>
<td>Cadmium</td>
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<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>Calcium</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>Chloride</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.01</td>
<td>0.02</td>
<td>0.5</td>
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<tr>
<td>Chromium</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.01</td>
<td>0.02</td>
<td>0.5</td>
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<tr>
<td>Cobalt</td>
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<td>0.5</td>
<td>0.1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
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<td>Copper</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
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<tr>
<td>Gallium</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
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<tr>
<td>Germanium</td>
<td>0.05</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
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<td>0.5</td>
</tr>
<tr>
<td>Gold</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.05</td>
<td>0.5</td>
<td>0.5</td>
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<tr>
<td>Heavy Metals (As Pb)</td>
<td>0.3</td>
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<td>0.1</td>
<td>0.5</td>
<td>0.4</td>
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<td>Iron</td>
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<td>0.5</td>
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<td>Lithium</td>
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<td>Magnesium</td>
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<td>1.0</td>
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<td>Manganese</td>
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<td>0.5</td>
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<td>Nickel</td>
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<td>0.1</td>
<td>0.06</td>
<td>0.1</td>
<td>0.02</td>
<td>0.1</td>
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<td>Phosphate</td>
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<td>0.05</td>
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<td>0.5</td>
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<td>Potassium</td>
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<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Silicon</td>
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<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Silver</td>
<td>0.5</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Sodium</td>
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<td>1.0</td>
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<td>1.0</td>
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<td>Strontium</td>
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<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
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<tr>
<td>Sulfate</td>
<td>0.5</td>
<td>1.0</td>
<td>0.5</td>
<td>2.0</td>
<td>5.0</td>
<td>5.0</td>
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<tr>
<td>Sulfite</td>
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<td>0.8</td>
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<td>Tin</td>
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<td>Zinc</td>
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<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Proper Wet Etching Station

- Fume hood to remove gases
- Moveable shield to protect workers

Figure 6-5 A workstation for acid etching. Note the face shield to prevent splattering, the perforated top for fume control, the remote-controlled drain and aspirator for acid removal, and the arrangement of drain and exhaust systems.
Professional Wet Etch Tub

- Tub is full before wafers inserted (a)
- Quick dump after etching for massive change (b)
- Refilled with etchant (c)
Recirculating Wet Etch Tub

- Tubs made of Teflon
- Temperature controlled

Figure 6-4 Recirculating, filtered, temperature-controlled bath for the etching of microelectronic substrates.
Silicon Dioxide (Glass)

- Glass - silicon dioxide: SiO₂
- Used as a dielectric insulator between conductors
- Also gate dielectric in Mosfets
- Grown by Furnace oxidation (Wet/Dry)
- Also by Chemical Vapour Deposition
- Etched with HF containing solutions in reaction

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

- Depends on free fluorine

\[
\text{HF} \rightarrow \text{H}^+ + \text{F}^-
\]

- Note the free hydrogen produced
Buffered Oxide Etch of Glass

- Straight HF undercuts resist
- Straight HF also diffuses through resist
- Causes Adhesion loss on resist in long etches.
- Since etch rate depends on free F⁻ ions
- Can stabilize F level with adding Ammonium Fluoride NH₄F
- Enhance etch rate and stabilize PH level
- Creates Buffered Oxide Etch (BOE) or Buffered HF (BHF)
- Note increase in etch rate with temperature
Agitation Enhancement of Etching

- Diffusion limited process controlled by reactant/product
- Increased agitation adds reactant to surface, removes products
- Also removes hydrogen bubbles
- Ultrasonic sound generates controllable agitation

![Etch Rate Vs. Agitation for Undoped Oxide ref 89](Fig 8)
Agitation and Bubbles

• Agitation necessary to remove Hydrogen bubbles
• Bubbles become trapped in between lines/holes: blocks them: creates a bridge for lines or blocks holes
• Bubbles on surface leave layer behind sometimes called snowball

Figure 9.19 Hydrogen bubble blockage of etchant.
Deposited Doped Oxides

- Deposited oxides: high Boron, Phosphorous, Arsenic
- Makes glass "soft" for other operations
- Dopant can significantly affect etch rate
- Boron lowers etch rate initially, then raises when enough B

![Graph showing etch rate vs. mole % B₂O₅ in SiO₂](image-url)
Wet Etch Phosphosilicate Glass (PSG)

- Glass with high phosphorus
- used for layers between conductors
- BOE etch rate increases with P content
Arsenic Doped Glass

- Arsenic doping enhances etch rate
- Lower density of Glass, faster etch rate

**Figure 5**
ref 91
Etching and Undercutting

- Perfect etching would be anisotropic
- Would generate Vertical sidewalls (c)
- Isotropic etch gets undercutting of resists
  removal of material under resist edge
- Because etch rate differs across wafer
  Undercutting different across wafer

Fig. 5 Comparison of (b) isotropic, and (c) completely anisotropic etching.
Isotropic Wet Etching and Feature Size

- Isotropic etch proceeds at same rate "r" in all directions
- Removes more at top edge than bottom
- Thus create circular profile of etch with radius

\[ R = rt \]

where \( t = \) time of etch (sec)

\( r = \) etch rate (microns/sec)

- Bottom of hole is flat, but edges curved
- Incomplete etch: film layer not fully removed

Figure 6-1 Isotropic etching in a wet chemical bath. (a) Unetched, masked film, showing parameters to be used. (b) Partially etched film, etch time \( t_1 \).
Isotropic Wet Etching and Feature Size

- Perfect etch then just clear bottom
- Time of perfect etch is

\[ \tau = \frac{z}{r} \]

where \( z \) = film thickness

- This generates minimum undercut
- Side of lines measured at top/bottom
- For perfect etch get line size at top

\[ x = x_L - 2rt \]

- But unevenness of etch over wafer means must have some overetch (eg 5-10%) at points
- Overetch generates undercut at top: same formula
- Significant undercut at bottom

\[ x = x_L - 2\sqrt{(rt)^2 - z^2} \]

(c) Ideally etched film, etch time \( \tau = z/r \). (d) Film after overetch, etch time \( t > \tau \).
Compensation for Undercut

- Even with ideal isotropic etch get undercut
- Bloat (expand) feature to compensate for undercut
- Set bloat to compensate for difference across wafer
- Resist is also etched, changing resist profile after etching
- Ideally want perfect "etch stop": layer below that does not etch

FIGURE 10
A schematic representation of some commonly observed etched profiles: (a) purely isotropic etch, (b) isotropic etch with a compensated mask, (c) anisotropic etch with no horizontal component, (d) isotropic etch with overetch, and (e) isotropic etch with isotropic etching of the mask.
Etch Stops and Hole Undercut

- Layer below generally does etch small amount
- Use an etch which slowly attacks "etch stop layer"
- Etch stop much better than timed etch
- Still get some etching into stop layer
- Holes open more at top than at bottom
- May bloat holes to make certain open

![Diagram of etch stops and hole undercut](image)

Figure 11.6 Wet-etch undercut profiles: dimensional control problem in (a) door etching\(^1\) and (b) window etching.\(^2\)
Overetch Profile

- Initial undercut nearly circular
- As proceeds undercut get more vertical
- Difference between top an bottom reduced

Fig. 6 (a) Isotropic etching of a film vs time ($L_R = 1$). Overetching results in profiles are more vertical. (b) Etching of film versus time when $L_R = 0.1$. (c) Etch bias is a measure of the amount by which the etched film undercuts the mask at the mask film interface. Fig. (c) Copyright, 1983, Bell Telephone Laboratories, Incorporated, reprinted by permission.
**Sloped Sidewalls**

- Sometimes want sloped sidewalls: sloped edges
- Easier for layers stepping over edge
- As wet etch undercuts resist begins to lift off.
- May deposit thin fast etch layer under mask
- Generates shallow slope in undercut

---

**Fig. 12** Different etch profiles produced from various degrees of undercutting during wet etch. (a) Good mask-to-film adhesion. (b) Undercutting has occurred at mask-film interface. (c) Use of fast-etching film to achieve controlled undercutting\(^{14}\). Reprinted with permission of Academic Press.
**Etching Bilayer Film**

- Sometimes put down two layers: fast and slow etch
- Fast top layer undercuts with radius $R$

\[ R_f = r_f t \]

- Slow lower layer matches upper at top
- at bottom has its own etch radius

\[ R_s = r_s t \]

---

**Figure 6-2** Etching of a bilayer film. (a) Unetched, masked film. (b) Generation of a sloped profile as the fast-etching surface layer recedes. $\beta$ defines the slope of the edge; $S'$ is a typical path by which etchant reaches the sloped area.
**Edge Residue and Etching**

- When film II steps over film I edge
  - film II thicker at edge
- More difficult to etch because thicker
- Result often leave residue at edge
- Isotropic wet etch does less of this.

![Diagram showing edge residue and etching](image)

*Fig. 9* If etching is anisotropic, overetching is needed to remove residual materials at steps. The degree of anisotropy, $A = 1$ in the example shown. Copyright, 1983, Bell Telephone Laboratories, Incorporated, reprinted by permission.
Silicon Nitride

- Nitride of silicon: $\text{Si}_3\text{N}_4$
- Used as a dielectric insulator between conductors
- Also gate dielectric in Mosfets
- Grown by Chemical Vapour Deposition
- Usually non-stoichiometric (not proper composition ratio)
  $\text{Si}_x\text{N}$ or $\text{Si}_x\text{N}_y\text{H}_z$
- Also grow Silicon Oxynitrides
  $\text{Si}_x\text{O}_y\text{N}_z$
- Very slow etching relative to oxide
Silicon Nitride Etches

- HF poor for Nitride, fast for oxide
  Bad: generally have oxide near nitride
- Means can use nitride as a mask for oxide in BOE etch
- Phosphoric Acid solutions $H_3PO_4$ best

**Silicon Nitride Etches**

**Table 6**

<table>
<thead>
<tr>
<th>Formula</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 HF</td>
<td>$22^\circ C$ 140-1000A/min depending on the nitride deposition method</td>
</tr>
<tr>
<td>2 28 ml HF, 170 ml $H_2O$, 113 g $NH_4F$</td>
<td>$22^\circ C$ BHF 5-10A/min</td>
</tr>
<tr>
<td>3 49% HF, 70% $HNO_3$</td>
<td>$70^\circ C$</td>
</tr>
<tr>
<td>4 Molten NaOH</td>
<td>$450^\circ C$</td>
</tr>
<tr>
<td>5 1-6 ml $HBF_4$, 100 ml $H_3PO_4$</td>
<td>$105^\circ C$ 1 ml to 100 ml has a 1:1 etch rate vs $SiO_2$, at $110^\circ C$ etches $1000$ A/min, resist compatible if post baked 140 to $160^\circ C$</td>
</tr>
<tr>
<td>6 $H_3PO_4$</td>
<td>140-200 C, Reflux Boiling $SiO_2$ etch masks. See Fig. 8</td>
</tr>
</tbody>
</table>
Nitride Etch with Boiling Phosphoric Acid $\text{H}_3\text{PO}_4$

- Etches nitride mostly fast
- Resist does lift during etch
- Poor etch of oxide:
- thus often use oxide as a mask for nitride

![Graph: Silicon Nitride Etch Rate in Boiling Phosphoric Acid](image)