Etching Techniques in Nanotechnology

Shashi Poddar
Etching is an important process in SEMICONDUCTOR FAB

GATE METAL WIDTH defines technology node

A typical computer processor involves close to half a billion of such transistors. Other active elements of any digital or analog device is also based on large scale integration of transistors in some form or the other.

e.g: DRAM, CMOS, NAND Flash

So where are we now?.....7 nm node

Where are we headed?
5 nm node using EUVL 2020 mass priduction
Bulk micromachining

- Silicon etched
- Silicon wafer
- SiO$_2$
- Isotropic etch
- Anisotropic etch
- Silicon wafer
**Etching**: Chemical reaction resulting in the removal of material

- **Wet etching**: etchants in liquid form
- **Dry etching**: etchants contained is gas or **plasma**
  - ionized gas

**Etch rate**: material removed per time (μm/min)
Selectivity and undercutting

Selectivity:

- etch rate of one material compared to another
- etch rate of one crystalline direction compared to another

Undercutting:

SEM image of a SiO$_2$ cantilever formed by undercutting (S. Mohana Sundaram and A. Ghosh, Department of Physics, Indian Institute of Science, Bangalore)
Application and properties of different wet etchants

<table>
<thead>
<tr>
<th>Etchant</th>
<th>Application</th>
<th>Etch Rate (s)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>48% HF</td>
<td></td>
<td>nm/min</td>
<td>for Si</td>
</tr>
<tr>
<td>Buffered oxide etch (BOE) (28 mL HF/113 g NH₄F/170 mL H₂O)</td>
<td></td>
<td>nm/min (25°C)</td>
<td></td>
</tr>
<tr>
<td>Poly etch</td>
<td></td>
<td>µm/min (25°C)</td>
<td></td>
</tr>
<tr>
<td>HF/HNO₃/HC₂H₃O₂ 8/75/17 (v/v/v)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KOH (44 g/100 mL)</td>
<td></td>
<td>µm/min (80°C)</td>
<td>Å/min SiO₂</td>
</tr>
<tr>
<td>Tetramethylammonium hydroxide (TMAH) (22 wt%)</td>
<td></td>
<td>µm/min (90°C)</td>
<td>SiO₂ virtually unreac-</td>
</tr>
</tbody>
</table>

High HF tends to etch SiO₂

Acidic etchants tend to etch Si isotropically

Basic etchants tend to etch Si anisotropically

Depend on concentration and temperature
Rate versus diffusion limited etching

Rate limited reactions are preferred → easier to control and more repeatable.
Isotropic etching

Estimate of etch depth

depth $\approx \frac{(D-d)}{2}$

- Etch rate is the same in all directions
- Typically acidic
- Room temperature
- Isotropy is due to the fast chemical reactions
- $X \, \mu\text{m/min}$ to $XX \, \mu\text{m/min}$

$\Rightarrow$ Reaction or diffusion limited?
Anisotropic etching

- Etch rate is different for different crystal plane directions
- Typically basic etchants
- Elevated temperatures (70-120°C)
- Different theories propose for anisotropy
- Slower etch rates, ~ 1 μm/min → Reaction or diffusion limited?

- Etch depths depend on geometry
- Undercutting also depends on geometry
<table>
<thead>
<tr>
<th>Etchant</th>
<th>Temperature (°C)</th>
<th>Si etch rate (μm/min)</th>
<th>({111}/{100}) selectivity</th>
<th>SiO(_2) etch rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH (40-50 wt%)</td>
<td></td>
<td></td>
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<tr>
<td>EDP (750ml Ethylenediamine 120g Pyrochatechol, 100 ml water)</td>
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<td></td>
</tr>
<tr>
<td>TMAH (Tetramethylammonium hydroxide 22 wt%)</td>
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</tbody>
</table>
Theories for anisotropic etching

The lower reaction rate for the {111} planes is caused by the larger activation energy required to break bonds behind the etch plane. This is due to the larger bond density of silicon atoms behind the {111} plane.

1 dangling bond

2 dangling bonds

Silicon lattice

(100)

(111)

The lower reaction rate for the {111} planes is caused by the larger activation energy required to break bonds behind the etch plane. This is due to the larger bond density of silicon atoms behind the {111} plane.
Theories for anisotropic etching of Si in aqueous based basic solvents

- Reduciton of water believed to be the rate determining step
- OH\(^-\) believed to be provided by H\(_2\)O near Si surface

\[
\text{SiOH}_2^{++} + 4\ e^- + 4\ H_2O \rightarrow \text{Si(OH)}_6^{--} + 2\ H_2 \quad \text{(reduction step)}
\]
Self-limiting etch and undercutting

- Intersection of \{111\} planes can cause **self-limiting** etch.
- Only works with concave corners

Resulting undercutting can be used to create suspended structures.
**Etch stop**: Technique to actively stop the etching process

- **Self-limiting etch**
- **Timed etch**
- **Insulator etch stop**
  - insulting layer
- **Etch stop via doping**
  - p-n junction
Etch stop via doping

Boron etch stop

\[
\text{SiOH}_2^{++} + 4 \, e^- + 4 \, \text{H}_2\text{O} \rightarrow \text{Si(OH)}_6^{--} + 2 \, \text{H}_2
\]

(reduction step)

- n type wafer heavily doped with B (called a p+ wafer)
- p-n junction
- p region Si deficient in e⁻
Etch stop via doping

**Electrochemical etch stop (ECE)**

\[
\text{SiOH}_2^{++} + 4\, e^- + 4\, \text{H}_2\text{O} \rightarrow \text{Si(OH)}_6^{--} + 2\, \text{H}_2
\]

(reduction step)

“Reverse bias” voltage applied to p-n junction keeps current from flowing
**Dry etching**

**Etching:** Chemical reaction resulting in the removal of material

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**Plasma etching:** mostly chemical etching

**Reactive ion etching (RIE):**

- In addition to the chemical etching, accelerated ions also physically etch the surface

Chemically reactive gas formed by collision of
- molecules of reactive gas with
- energetic electrons
- Excited/ignited be RF (radio frequency) electric field $\sim 10$-15 MHz
Reactive ion etching

Plasma hits surface with large energy

- In addition to the chemical reaction, there is physical etching
- Can be very directional—can create tall, skinny channels

If there is no chemical reaction at all, the technique is called ion milling.
<table>
<thead>
<tr>
<th>Material</th>
<th>Reactive gas</th>
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<tbody>
<tr>
<td>Silicon (Crystalline or polysilicon)</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
</tr>
<tr>
<td>Si₃N₄</td>
<td></td>
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<tr>
<td>Photoresist</td>
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</table>
Deep reactive ion etching (DRIE)

Bosch process

- 1st, reactive ion etching step takes place
- 2nd, fluorocarbon polymer deposited to protect sidewalls

Kane Miller, Mingxiao Li, Kevin M Walsh and Xiao-An Fu, The effects of DRIE operational parameters on vertically aligned micropillar arrays, Journal of Micromechanics and Microengineering, 23 (3)